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Research Article

Reduction of Peroxide Value and Free Fatty Acid Value of Used Frying Oil Using TiO_2 Thin Film Photocatalyst

Ummi Kaltsum[1]*, Affandi Faisal Kurniawan[1], Iis Nurhasanah[2], P. Priyono[2]

[1]*Physics Education Department, Universitas PGRI Semarang, Jln. Sidodadi Timur No.24, Semarang 50125, Indonesia*
[2]*Physics Department, Universitas Diponegoro, Jl. Prof. Soedarto, Kampus Undip Tembalang, Semarang 50239, Indonesia*

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Abstract

The quality of used frying oil degraded due to the presence of products degradation, such as; PV and FFA which formed during the frying process. PV and FFA are harmful to human health. The photocatalytic activity of TiO_2 thin film has been applied in various fields, especially in the environment. The aim of this study is to evaluate photocatalytic activity of TiO_2 thin film for reducing PV and FFA in used frying oil. The TiO_2 thin films were deposited on glass substrate by spray coating method at a temperature of 450 °C. The TiO_2 precursor solution was prepared by mixing TTiP, AcAc, and ethanol. The thin films were varied into two conditions; as-deposited and annealed at a temperature of 500 °C. The morphology, crystalline structure, and optical properties of the thin films were characterized by scanning electron microscope (SEM), X-ray Diffraction (XRD), and UV-VIS spectrophotometer, respectively. Photocatalytic process was carried out by putting TiO_2 thin film in used frying oil and irradiated by sunlight. The result showed that both of TiO_2 thin films were still amorphous in nature. However, there was a peak with low intensity for annealed TiO_2 thin film which corresponding to the TiO_2 anatase crystals plane of (101). Annealing process improved crystallinity and changed the shape morphology of TiO_2 thin films. The band gap was found to be 3.59 eV for as-deposited TiO_2 thin film and 3.49 eV for the annealed-TiO_2 thin film. Photocatalytic process shows that TiO_2 thin films reduced FFA and PV of used frying oil up to 67.10% and 79.15%, respectively. The photocatalytic activity of annealed TiO_2 thin film was higher than as-deposited TiO_2 thin film. The results indicated that TiO_2 thin film photocatalyst potential as the new alternative method to purify used frying oil.

Keywords: annealing; FFA; PV; TiO_2; used frying oil

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1. Introduction

Cooking oil is a foodstuff that has a main composition of triglycerides and made from plant, animal, or synthetic fat. The main function of cooking oil is used for frying food. At the room temperature, the cooking oil is typically liquid, but certain oil that contains high saturated fat is solid, such as palm oil [1]. In Indonesia, most of the frying oil made from palm oil. Some of the psychochemical properties of frying oil are density, viscosity, boiling point, iodine value, saponification value, peroxide

* Corresponding Author.
E-mail: um_mik@yahoo.co.id
Telp.: +62-24-8316377 Fax.: +62-24-8448217

value (PV), and free fatty acid (FFA) value [2]. Several factors, such as: heat, air and moisture, resulting in polymerization, oxidation and hydrolysis, changed the psychochemical properties and degraded the frying oil quality [3]. During the frying process, triglyceride converted into degradation products, such as: FFA, peroxide and total polar material (TPM). The existence of degradation products decreased the quality of frying oil. The quality degradation of frying oil is characterized by increasing in FFA, PV, polar material, viscosity and foam, discoloration, low smoke point, and low iodine value [4]. The degradation products contain in used frying oil are harmful to human health if consumed [5]. The consumption of used frying oil causes various diseases i.e. metabolic changes [6], hypertension [7], coronary heart disease [8], and cancer [9].

The membrane filtration method is the main technology which has been used for purifying used frying oil. The uses of bagasse adsorbent have succeeded in reducing PV up to 26.67 % [10] and FFA up to 82.14 % in frying oil [11]. The other adsorbent, magnesol adsorbent, also could degrade TPM in frying oil [12]. In addition, two phases supercritical carbon dioxide extraction was able to purify triglycerides from frying oil [13]. However, these technologies need preparation and pretreatment of sample, a lot of equipment, and many steps to do.

Since the discovery photocatalytic property by Fujishima and Honda in 1972, titanium dioxide (TiO_2) has been widely used in many field applications. The most TiO_2 applications are water purification from organic pollutant [14], water disinfection from contaminated pathogenic micro-organisms [15], and air purification from nitrogen oxides, volatile hydrocarbons and chlorohydrocarbons, odorous compounds, microbes, fungi, etc. [16]. Compared to other semiconductor materials TiO_2 has several advantages; cheap, non-toxic, high photo activity, easily recycled, inert, and self-regeneration [17].

The photocatalytic activity of TiO_2 thin film for purifying process can be explained by the mechanism as follows. When the thin film is irradiated by sunlight (photon), electron in valence band excites to conduction band and produces conduction electron and hole. Conduction electron and hole react with compounds produce radicals that degrade the organic pollutant in compounds [18]. Based on those mechanisms, TiO_2 thin film is also potential to reduce the degradation products in used frying oil. Therefore, the photocatalytic activity of TiO_2 thin film is suitable as a new alternative technology for purifying used frying oil with simple equipment and process.

Aim of this study is to investigate potential application of TiO_2 thin film photocatalyst for purifying used frying oil. The value of PV and FFA in used frying oil were analyzed after photocatalyst process using TiO_2 thin film under sunlight irradiation. Reduction of the value of FFA and PV were correlated to photocatalytic activity of TiO_2 thin films.

2. Materials and Method

The main steps of deposit TiO_2 thin films were cleaning substrate, preparation of precursor solution, and deposition of solution onto substrate. The TiO_2 thin films were deposited on microscope glass by spray coating at temperature of 450 ^{o}C. The glass substrate was cleaned with detergent, hydrochloride acid (HCl), acetone, and distilled water for 5 minutes, respectively. The procedure to prepare the precursor solution of TiO_2 thin films used in this research based on the procedure as was described in the literature [19]. We made some modifications in spraying process of precursor solution onto a substrate. The precursor solution of TiO_2 thin films was made by mixing 0.2 M of titanium(IV) isopropoxide (TTiP, purity 97%), 0.4 M of acetylacetone (AcAc, purity 99%), and ethanol as solvent. The mixing of precursor solution was carried out using magnetic stirrer for 2 hours. The spraying process was performed by one minute of spray followed by one minute of pause. One of deposited thin film was annealed at temperature of 500 ^{o}C for 2 hours.

The properties of thin films were characterized using Scanning Electron Microscope (SEM), X-ray diffraction (XRD), and UV-VIS spectrophotometer. The morphology and thickness of TiO_2 thin film were investigated using JEOL JSM-6510 LA Scanning Electron Microscope (SEM). Crystalline structure was analyzed using MAXima_X XRD-7000X-ray diffractometer. The optical transmittance was measured by Shimadzu 1240 UV-visible spectrophotometer and then used to determine band gap energy. The photocatalytic process to purify used frying oil was conducted by putting TiO_2 thin film into used frying oil and irradiated by sunlight for 5 hours. The values of FFA and PV of used frying oil were measured using titration method before and after irradiation.

3. Results and Discussion

3.1. Morphology and structural properties

The surface morphology of as-deposited and annealed TiO_2 thin films is shown in Figure 1. It can be seen that as-deposited TiO_2 thin film consists of spherical-like grains with average sizes of around 0.5 μm, whereas annealed TiO_2 thin film is constructed with plate-like thin layer with average sizes of around 1.0 μm. The existence of plate thin layer leads roughness surface. In addition, the film thickness is estimated from cross-sectional SEM images to be 43 nm for as-deposited TiO_2 thin film and 24 nm for annealed TiO_2 thin film. It is suggested that annealing treatment results in change of surface morphology as well as the film roughness and affects film thickness. The same result was also showed by Senain *et al*. [20] and Hanini *et al*. [21] that the thickness of as-deposited thin film was larger than annealed thin film.

Figure 2 shows the XRD patterns of as-deposited and annealed TiO_2 thin films. The large bump exists in both XRD patterns which indicate that TiO_2 thin films are amorphous. However, there is a weak peak at 25.78^o observed in annealed TiO_2 thin film. That peak is corresponded to (101) plane of TiO_2 anatase. It shows that annealing process at 500 ^oC leads the beginning formation of TiO_2 anatase and improved the crystallinity of films [20,21].

3.2. Optical properties

The optical properties of TiO_2 thin film were investigated by UV-Vis absorption spectrum, as shown in Figure 3. Both of thin films show similar absorption properties, but the absorption of annealed TiO_2 thin film is slightly larger than as-deposited TiO_2 thin film. Strong absorption observed in the ultra-violet range of 280-315 nm with peak absorption at 307 nm. In addition, the low absorption observed in the visible range of 380-600 nm for as-deposited thin film and 360-500 nm for annealed thin film. This meant both of thin film could absorb uv-light and visible light. Band gap energy of TiO_2 thin film can be determined by plotting the absorption coefficient to the photon energy using Equation (1) [22].

$$\alpha h\upsilon = A\left(h\upsilon - E_g\right)^{1/2} \tag{1}$$

where α is absorption coefficient, A is constant, $h\upsilon$ is photon energy, and E_g is band gap energy.

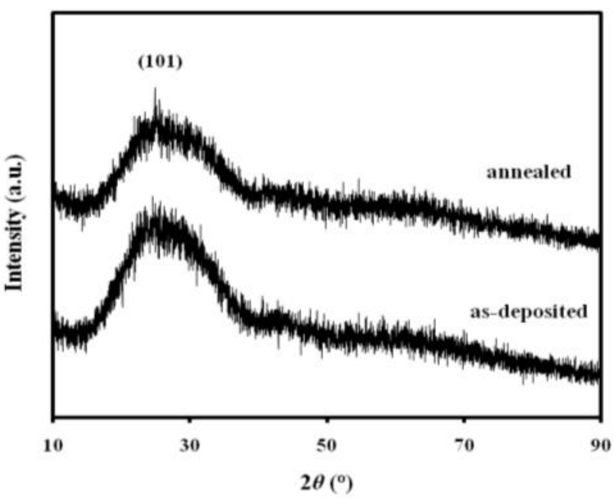

Figure 2. XRD pattern of as-deposited and annealed TiO_2 thin film

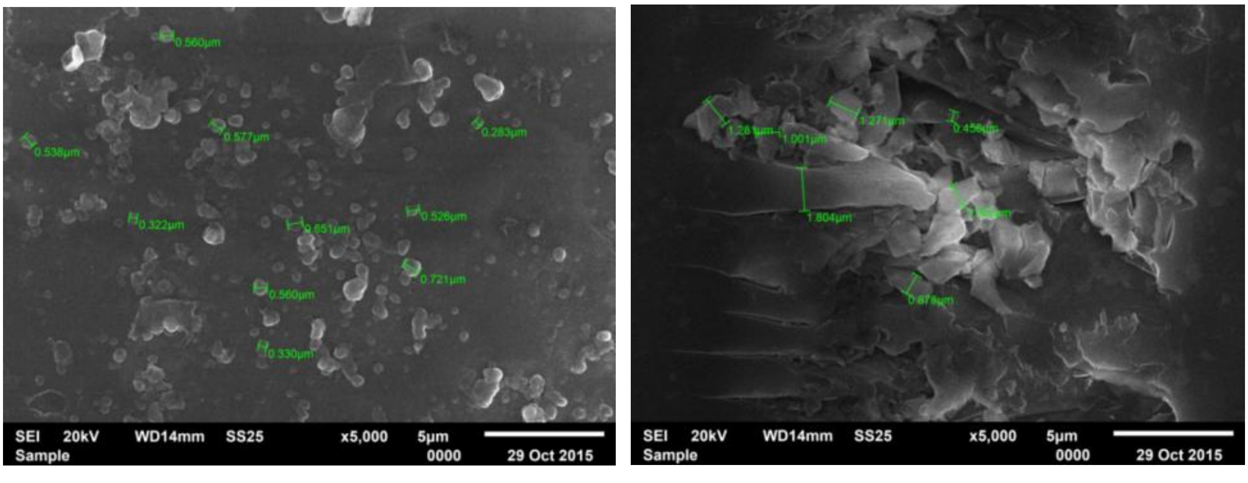

Figure 1. The SEM images of TiO_2 thin film (a) as-deposited and (b) annealed

Absorption coefficient α can be determined using Equation (2) [22].

$$\alpha = \frac{A}{d} \qquad (2)$$

where A and d are absorbance and thickness film, respectively. The extrapolation of the linear part of the curve to the *x*-axis results in the band gap energy [23]. Band gap energy of as-deposited thin film and annealed thin film werefound 3.59 eV and 3.49 eV, respectively as shown in Figure 4. Those results are greater than the bulk of TiO_2 (3.2 eV) as was found by Agbo *et al.* [24]. Furthermore, the annealing process lead to decrease the band gap of TiO_2 thin film. Similar phenomenon was also reported by Hanini *et al.* [21], Agbo *et al.* [24], Tian *et al.* [25], and Habib *et al.* [26].

3.3. Photocatalytic properties of TiO_2 thin films

It is well known that TiO_2 have strong photocatalytic activity when irradiated by ultra-violet ray. The photocatalytic properties of TiO_2 thin films were examined to purify used frying oil by determining the parameter quality of oil i.e. FFA and PV before and after sunlight irradiation for 5 hours. Figure 5 shows FFA percentage of used frying oil before and after sunlight irradiation. Sunlight irradiation caused decrease in the percentage of FFA used frying oil. Low FFA reduction was found when used frying oil only irradiated by sunlight without TiO_2 thin film. Otherwise, large FFA reduction appears for used frying oil with TiO_2 thin films. It indicates that TiO_2 thin films degrade FFA value of used frying oil. The degradation of FFA value of used frying oil after irradiation without TiO_2 thin film is 1.73 %. On the other hand, the degradation of FFA value of used frying oil after irradiation was found 54.98% for as-deposited thin film, and 67.10 % for annealed thin film. A similar degradation was also observed in the PV of used frying oil as depicted in Figure 6. The PV degradation of 12.74 % obtained after irradiation for used frying oil without TiO_2 thin film, 78.03 % for as-deposited thin film, and 79.15 % for annealed thin film. The results demonstrated that reduction of FFA and PV was higher in frying oil with TiO_2 thin film than frying oil without TiO_2 thin film and the highest reduction was obtained for annealed thin film.

The existence of TiO_2 thin film enhanced the degradation of FFA and PV in frying oil. It is suggested that thin film acted as a catalyst that enhanced degradation of FFA and PV by photo-

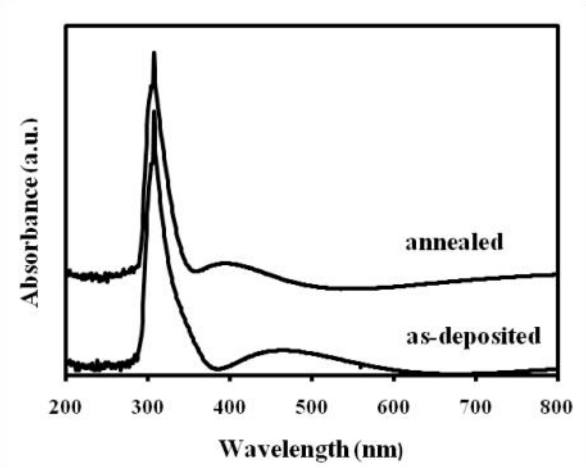

Figure 3. The absorbance spectrum of as-deposited and annealed TiO_2 thin film

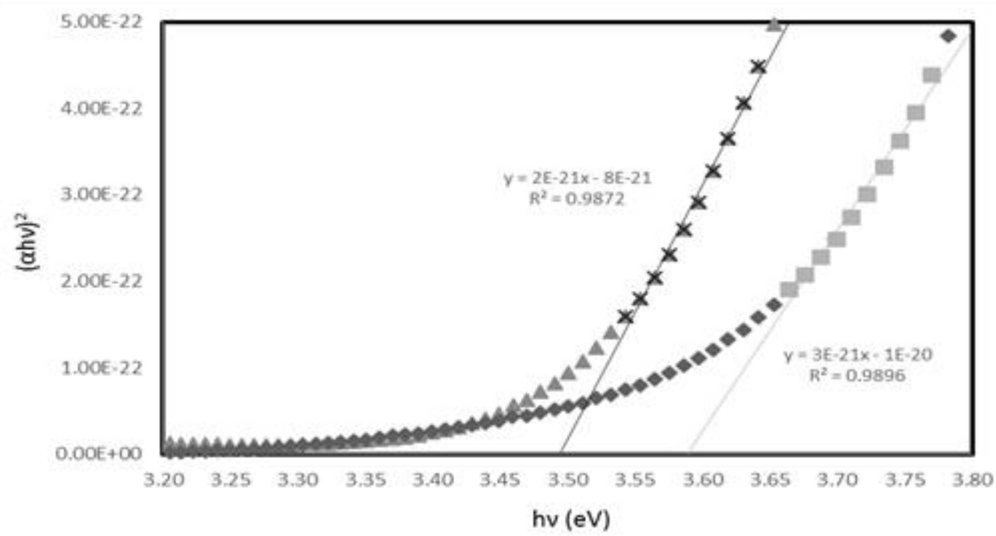

Figure 4. Plots of $(ahv)^2$ versus photon energy (hv) of TiO_2 thin film

catalytic process (photodegradation). The photodegradation of FFA and PV in used frying oil could be explained by the following mechanism. Electrons in valence band is excited to the conduction band and produce conduction electron (e^-_{cb}) and holes in the valence band (h^+_{vb}) when TiO_2 thin film irradiated by sun light (photon) as shown in Equation (3) [18]. Electrons and holes reacted with carboxylic acid produced hydrogen radical (H•) and hydrocarbon radical (R•) as shown in Equation (4) and Equation (5), respectively [27]. Finally, the hydrogen radical and hydrocarbon radical interacted with frying oil degradation products (peroxides and FFA), so the amount of degradation products in used frying oil reduced. Carboxyl group is a fatty acid group, in which the fatty acid as the main component of frying oil. The all steps were summarized in the following equations:

$$TiO_2 + h\upsilon(\text{photon}) \rightarrow e^-_{cb} + h^+_{vb} \quad (3)$$

$$RCOOH + e^-_{cb} \rightarrow H\bullet + RCO_2^- \quad (4)$$

$$RCO_2^- + h^+_{vb} \rightarrow R\bullet + CO_2 \quad (5)$$

Annealed TiO_2 thin film possesses better photocatalytic activity than as-deposited thin film. It is due to difference morphology, structural and optical properties of thin film caused by annealing treatment which influences photocatalytic activity [28]. In our research, annealed thin film had plate-like morphology that represent larger surface. Large surface of thin film was potential to adsorb much frying oil [29]. This produced more hydrogen radical and hydrocarbon radical that reacted with the degradation products.Annealing treatment also lead to increase Ti^{3+} concentration in the lattice of TiO_2. Increasing of Ti^{3+} concentration improved the film crystallinity which was characterized by an emerging diffraction peak as shown in Figure 2. The Ti^{3+} forms a donor level between the band gap of TiO_2 can act as trapper electron that reduce the recombination of photo degenerated electrons and holes [30].

Annealed thin film was thinner than as-deposited thin film, so that more light was absorbed and more conduction electron was produced. The absorbance of annealed thin film was slightly larger than absorbance of as-deposited thin film as shown in Figure 3. The band gap energy of annealed thin film was smaller than as-deposited thin film as shown Figure 4. The small band gap energy leads to small photon energy required to excite electron (conduction electron). Therefore, the number of conduction electrons as well as hole which generated in annealed thin film more than as-deposited thin film. This resulted in increasing number of hydrogen radical and hydrocarbon radical formation that reduces degradation products. Annealing treatment increased photocatalytic activity of TiO_2 thin film that resulted better photodegradation [21]. The decreasing of degradation product in used frying oil means the increasing of photodegradation of TiO_2 thin film and improves the quality of frying oil.

4. Conclusions

The TiO_2 thin films have been deposited by spray coating method. The properties of as-deposited thin film were spherical-like grains with average sizes of around 0.5 μm, band gap energy of 3.59 eV, and amorphous structure. The annealed thin film possesses plate-like morphology with average sizes of around 1.0

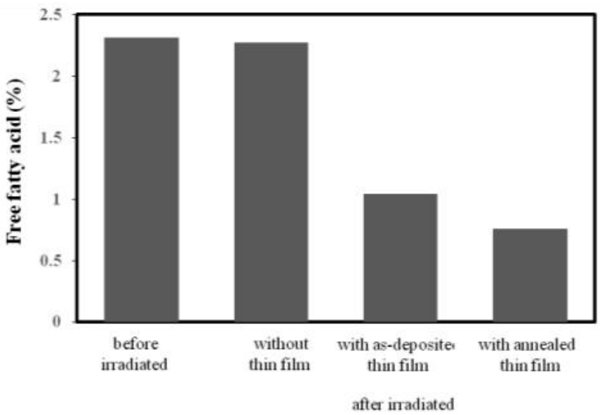

Figure 5. Free fatty acid of used frying oil before and after irradiated by sun light

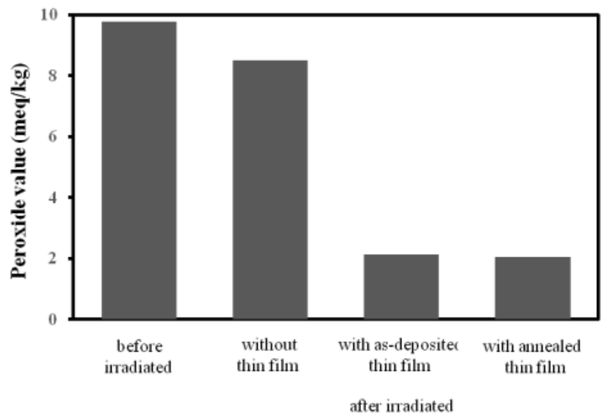

Figure 6. Peroxide value of used frying oil before and after irradiated by sun light

μm, band gap of 3.49 eV, and amorphous structure. The TiO_2 thin films reduced FFA and PV value in the used frying oil up to 67.10% and 79.15%, respectively. The photodegradation of annealed thin film was higher than as-deposited TiO_2 thin film. TiO_2 thin film photocatalyst potential as alternative method for purifying of used frying oil.

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References

[1] Behrman, E., Jang, G.V. (2005). Cholesterol and Plants. *Journal of Chemical Education*, 82 (12): 1791-1793

[2] Zahir, E., Saeed, R., Abdul, H.M, Yousuf, A. (2014). Study of physicochemical properties of edible oil and evaluation of frying oil quality by Fourier Transform Infrared (FT-IR) Spectroscopy. *Arabian Journal of Chemistry*, Article In Press.

[3] Gebhardt, B. (1996). Oils and Fats in Snack Foods. New York, USA: John Wiley & Sons Inc.

[4] Soh, K.H., Soo, M.C., Yuen, M.C. (2006). Oxidative Stability and Storage Behavior of Fatty Acid Methyl Esters Derived from Used Palm Oil. *Journal of the American Oil Chemists' Society*, 83: 947-952.

[5] Bhattacharya, A.B., Sajilata, M.G., Tiwari, S.R., Singhal, R. (2008). Regeneration of Thermally Polymerized Frying Oils with Adsorbents. *Food Chemistry*, 110: 562-570.

[6] Chiang, Y.F., Shaw, H.M., Yang, M.F. Huang, C.Y., Hsieh, C.H., Chao, P.M. (2011). Dietary Oxidised Frying Oil Causes Oxidative Damage of Pancreatic Islets and Impairment of Insulin Secretion, Effects Associated with Vitamin E Deficiency. *British Journal of Nutrition*, 105: 1311-1319.

[7] Chun, Y.N., Yusof, K., Othman, Zakiah, J., Hj.Mohd, S.Q., Kamsiah, J. (2012). Involvement of Inflammation and Adverse Vascular Remodelling in the Blood Pressure Raising Effect of Repeatedly Heated Palm Oil in Rats. *International Journal of Vascular Medicine*, Article ID 404025.

[8] Kummerow, F.A. (2013). Interaction between Sphingomyelin and OxysterolsContributes to Atherosclerosis and Sudden Death. *American Journal of Cardiovascular Desease*, 3: 17-26.

[9] Chopra, M., Schrenk, D. (2011). Dioxintoxicity, Aryl Hydrocarbon Receptor Signaling, and Apoptosis-Persistent Pollutants Affect Programmed Cell Death. *Critical Review in Toxycology*, 41(4): 292-320.

[10] Wannahari, R., Nordin, M.F.N. (2012a). Reduction of Peroxide Value in Used Palm Cooking Oil Using Bagasse Adsorbent. *American International Journal of Contemporary Research*, 2(1): 185-191.

[11] Wannahari, R., Nordin, M.F.N. (2012b). The Recovery of Used Palm Cooking Oil Using Bagasse as Adsorbent. *American Journal of Engineering and Applied Science*, 5(1): 59-62.

[12] Somnuk, C., Bhundit, I., Chanin, T. (2013). Cytotoxicity of Used Frying Oil Recovered by Different Adsorbents. *Kasetsart Journal*, 47: 874 – 884.

[13] Jungro, Y., Byung, S.H., Yun, C.K., Kong, H.K., Mun, Y.J., Yung, A.K. (2000). Purification of Used Frying Oil by Supercritical Carbon Dioxide Extraction. *Food Chemistry*, 71(2): 275-279.

[14] Sobczynski, A., Dobosz, A. (2001). Water Purification by Photocatalysis on Semiconductors. *Polish Journal of Environmental Studies*, 10(4): 195-205.

[15] Cathy, M., Jeanette, M.C.R., Detlef, W.B., Peter, K.J.R. (2007). The Application of TiO_2 Photocatalysis for Disinfection of Water Contaminated with Pathogenic Micro-Organisms: A Review. *Research on Chemical Intermediates*, 33(3): 359-375.

[16] Miller, R., Fox, R. (1993). Treatment of Organic Contaminants in Air by Photo-catalytic Oxidation: A Commer-cialization Perspective, in: Photo-catalytic Purification and Treatment of Water and Air. In *Proceedings of the 1st International Conference on TiO_2*, 573-578. D. Ollis, H. Al-Ekabi, (ed:) International Conference on TiO_2.

[17] Charp, O., Huisman, C.L., Reller, A. (2004). Photoinduced Reactivity of Titanium Dioxide. *Progress in Solid State Chemistry*, 32: 33-177.

[18] Luan, X., Wang, Y. (2014). Preparation and Photocatalytic Activity of Ag/Bamboo-Type TiO_2 Nanotube Composite Electrodes for Methylene Blue Degradation. *Materials Science in Semiconductor Processing*, 25: 43-51.

[19] Oja, A.I, Kiisk, V., Krunks, M., Sildos, I., Junolainen, A., Danilson, M., Mere, A., Mikli, V. (2012). Characterization of Samarium and Nitrogen Co-Doped TiO_2 Films by Chemical Spray Pyrolysis Prepared. *Applied Surface Science*, 261: 735-741.

[20] Senain, I., Nayan, N., Saim, H. (2010). Structural and Electrical Properties of TiO_2 Thin Film Derived from Sol-Gel Method Using Titanium (IV) Butoxide. *International Journal of Integrated Engineering*, 2(3): 29-35.

[21] Hanini, F., Bouabellou, A., Bouachiba, Y., Kermiche, F., Taabouche, A., Hemissi, M., Lakhdar, D. (2013). Structural, Optical and Electrical Properties of TiO_2 Thin Films Synthesized by Sol-Gel Technique. *IOSR Journal of Engineering*, 3(6): 21-28.

[22] Benhaoha, B., Rahal, A.,Benramache, S. (2014). The Structural, Optical and Electrical Properties of Nanocrystalline ZnO:Al Thin Films. *Superlattices and Microstructures*, 68: 38-47.

[23] Eiamchai, E., Pongpan, C., Artorn, P., and Pichet, L. (2009). A Spectroscopic Ellipsometry Study of TiO_2 Thin Films Prepared by Ion-Assisted Electron-Beam Evaporation. *Current Applied Physics*, 9(3): 707-712.

[24] Agbo, P.E., Nnabuchi, M.N., Onogu, K.O. (2012). Effect of Annealing on the Thickness and Band Gap of Novel Core-Shell Crystalline Thin Film. *Journal of Ovonic Research*, 8(5): 127-134.

[25] Tian, G.L., He, H.B., Shao, J.D. (2005). Effect of Microstructure of TiO_2 Thin Films on Optical Band Gap Energy. *Chinese Physical Society*, 22(7): 1787-1789.

[26] Habib, M.P., Woo, Y.K., Kwang, D.J., Oh-Shim, J. (2005). A Chemical Route to Room-Temperature Synthesis of Nanocrystalline TiO_2 Thin Films. *Applied Surface Science*, 246: 72-76.

[27] Kraeutler, B., Bard, A.J., (1978). Heterogeneous Photocatalytic Synthesis of Methane from Acetic Acid - New Kolbe Reaction Pathway. *J. Am. Chem. Soc.*, 100 (7): 2239-2240.

[28] Lin, C.P., Chen, H., Nakaruk, A., Koshy, P., Sorrell, C.C. (2013). Effect of Annealing Temperature on the Photocatalytic Activity of TiO2 Thin Films. *Energy Procedia*, 34: 627-636.

[29] Peerakiatkhajorn, P., Chawengkijwanich, C., Onreabroy, W., Chiarakorn, S. (2012). Novel Photocatalytic Ag/TiO_2 Thin Film on Polyvinyl Chloride for Gaseous BTEX Treatment. *Materials Science Forum*, 712: 133-145.

[30] Paz, Y., Heller, A. (1997). Photo-Oxidatively Self-Cleaning Transparent Titanium Dioxide Films on Soda Lime Glass: The Deleterious Effect of Sodium Contamination and Its Prevention. *Journal of Material Research*, 12: 2759-2766.