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Composite of Nano-TiO_2 with Cellulose Acetate Membrane from Nata de Coco (Nano-TiO_2/CA(NDC)) for Methyl Orange Degradation

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Abstract

Composite of nano-TiO_2 with cellulose acetate (CA) has been prepared in this research. The composite then was used as photocatalyst for methyl orange degradation. The cellulose acetate was produced from Nata de Coco (NDC). Immobilization of nano TiO_2 on the CA(NDC) membraneaims to increase the separation ability of photocatalyst after the degradation. TiO_2 nanoparticles were synthesized byalkaline destruction method with NaOH and it was followed by calcination at 450 °C. The membrane photocatalyst nano TiO_2-CA(NDC) was prepared by phase inversion method by mixing TiO_2 nanoparticles with the CA casting solution. Analysis by Scanning Electron Microscopy (SEM) indicates that nano TiO_2 has been successfully synthesized, and the average diameter are 88.63 nm ± 4.37. The X-ray diffraction pattern (XRD)of nano TiO_2 shows anatase TiO_2 as a major component. Photodegradation of methyl orange solution was conducted with nano-$TiO_2$and nano TiO_2-CA(NDC) at various times of 10, 20, 30, 40, and 50 minutes. Degradation was conducted by the batch system with UV light with 8 watts of power. The result shows that photodegradation reaction followed the second order. The rate constant of methyl orange degradation with nano TiO_2-CA(NDC) is 0.01±0.002 ppm.min^{-1}. Eventhough, the rate constant value is lower than the methyl orange degradation with nano-TiO_2 powder, however, the immobilized form offers an advantage of separation process from the treated solution. Statistical analysis also found that the difference in the rate constant is not siginificant. It means that the immobilization of nano-TiO_2 into a CA(NDC) membrane will not reduce the photocatalytic activity of TiO_2, even it will reduce the application cost due totheelimination of separation treatment.

1. Introduction

Photocatalytic degradation with titanium dioxide, TiO_2, recently known as an alternative for waste water treatment or a photocatalytic treatment of some organic contaminants such as dyes, hydrocarbon, pesticide and also pathogenic microbe[1]. Titanium dioxide also a promising photocatalyst for textile waste watertreatment. Dyes from textile industries is a non biodegradable contaminant, which is consist of azo compounds (-N=N) and its derivative with benzene molecules. One of the azo compounds is methyl orange. It is known as carsinogenic and mutagenic compounds[2]. Therefore, an effort to degrade that dye is important to reduce the hazardous of textile waste water.

TiO_2 is a material with high photocatalytic activity and good chemical stability even under extreme condition [3,4]. In addition, TiO_2 is non-toxic, inexpensive and has electrochemical ability to oxidize some organic pollutants and also reduce some metallic ions in wastewater [5]. Some efforts to engineer the TiO_2 have been conducted to enhance their performance as a catalyst, such as reduce the TiO_2 particle size into a nano-size particle [6]. It is known that the reduction of particle size capable of increasing the catalytic performance due to high surface area of interaction.

However, TiO_2 powder form a colloid when dispersed in water [7]. It could become a disadvantage especially on recovering process. It must be conducted by ultrafiltration or centrifugation [8]. Therefore, some researchers on immobilization of TiO_2 on some substrate have been conducted, such as on graphite [9], on titanium foil [10], carbon doped-nano TiO_2 [11]. An effort to impregnate TiO_2 on cellulose producing cellulose-TiO_2 nano-composite also has been conducted [12]. The resultingproof the feasibility of TiO_2 immobilization in porous cellulose for UV-activated dye degradation. Cellulose acetate, CA, is a promising candidate due to their high toughness, high biocompatibility, good desalting properties, high flux properties and also inexpensive. The CA membrane also has high hydrophilicity, in which this property is important in order to minimize fouling [13]. Theless fouling possibility has been proven through morphological analysis before and after permeability test [14].The CA membrane with TiO_2 nanoparticles inside also can be prepared easily by phase inversion method by dispersing the nanoparticles in the CA casting solution [15].

This research studies the application of CA membrane as a medium for nano TiO_2. Nata de Coco, NDC was used as raw material for CA production. CA membrane from NDC is known to have strong and flexibility properties. Aminzadeh et al. [16] found that the Thermogravimetric analysis, TGA, on CA and TiO_2 provide the similar degradation pattern. It indicates that CA may not affect the physical character of nano TiO_2. Therefore, in this research, the CA membrane from NDC was used as a medium for nano TiO_2. The photocatalytic performance of nano TiO_2-CA(NDC) was studied through its application in a Methyl Orange degradation in a batch reactor with ultraviolet light as a photon source.

2. **Experimental**

Chemicals used in this research were pro analysis grade, and those were used without further treatment. The chemicals were TiO_2 A-100 anatase (98%, Japan) , Ammonium sulphate (Merck), Sodium Hydroxide (Merck), acetic acid glacial (Merck), anhydrous acetate (98 %, Merck), sulphuric acid (Merck), Poly Ethylene Glycol 1000 (Merck), Methyl Orange (Merck), Acetone (Merck). Other components were coconut water, *Acetobacter xylinum*, nata de coco gel, and distilled water.

2.1 Synthesis of nano-TiO_2

The synthesis of nano-TiO_2 was conducted through destruction method with conventional heating under air atmosphere. 2 grams of anatase TiO_2 was mixed with 17.5 mL of 10 M NaOH [17]. The mixture was sonicated for 5 minutes then was put into Teflon tube and was heated on a hot plate at 150 ^oC for 24 hours. The result was washed with deionized water and continued with 0.1 M HCl solution. The washing treatment was conducted at the pH of the mixture was neutral. The mixture then was heated and calcined at 450 ^oC for 2 hours.

2.2. Preparation of cellulose acetate membrane from nata de coco (NDC)

Some sheets of NDC withathickness of 0.5 – 0.7 cm were dipped in a 4% NaOH solution for 24 hours to remove the bacteria remains. The sheets then were neutralized by soaking in a 4% of acetic acid glacial for 24 hours. Natalia[18] found that the 4% of NaOH solution and the 4% of acetic acid glacial solution were succesfully produce the cellulose acetate from NDC. In order to reduce the acid content in the sheets, those were soaked in a distilled water for 24 hours and followed by washing for many times until the color was back to white. The treated NDC sheets then were dried under sunlight for 3-4 days to produce dry NDC sheets. The dried NDC sheets then were blended to produce NDC powder.

The cellulose acetate, CA, was produced through 4 steps including swelling, acetylation, hydrolisis and purification [19]. The swelling step was a step in activation, in which the cellulose fibres were inflated withtheaddition of 64 mL of glacial acetate in every 8 grams of cellulose powder. The sweeling form would allowreagents to penetrate easier into cellulose fibres and it leads to the exchange of hydroxylation groups in the cellulose molecules with the acetyl groups in the anhydrous acetate. These are named as acetylation process to produce cellulose acetate [20]. The acetylaton process was conducted under 18 ^oC, because the reaction between the anhydrous acetate with the swelled cellulose was an exothermic process. Meanwhile, the hydrolisis process was the next step to eliminate the crystallinity of cellulose. The 67% oftheacetic acid solution was used for hydrolisis. The last step wasapurification, which was conducted thourgh centrifugation until a white sediment was formed in the bottom oftheflask. The white sediment was then washed with deionized water and was dried to produce the cellulose acetate powder.

2.3 Preparation of nano-TiO_2-CA(NDC) membrane

The membrane of nano TiO_2-CA(NDC) was synthesized by phase inversion method [15,21]. The cellulose acetate membrane was prepared from nata de coco, a natural product from coconut water.The phase inversion occurred between three phases that presence in the system, i.e., the polymer, solvent and non-solvent [15, 17]. The membrane was produced with the composition of polymer: acetone (as solvent) at a ratio of 17.5: 82.5 (weight %). The composition of the polymer was CA-NDC: nano TiO_2 at a ratio of 80:20 (weight %). This ratio was chosen as the optimum weight ratio of nano TiO_2 powder that can be mixed with CA-NDC powder. The mixture still can be casted and peeled out without any cracks. The nano-TiO_2 powder was dispersed in aceton and stirred for 4 hours. The dispersion then was sonicated for 10 minutes. Meanwhile, the prepared cellulose acetate, CA, was mixed with poly ethylene glycol, PEG, ataratio of CA:PEG 18:5 (weight %, the weight % was calculated from total solution). The mixture then was stirred for 24 hours. The membrane was molded in a glass. After being cast on the molding glass, the glass was then poured immediately into coagulation bath which was filled with non-solvent, which is distilled water, at 9 ^{o}C. The membrane formed than was washed with distilled water until reach neutral pH and then was dried.

2.4 The analysis of materials and Methyl Orange degradation

The prepared material was analyzed with XRD (Shimadzu 6000 at 2θ of 10 ^{o} – 80 ^{o} at 40 mA and 40 kV). Morphological analysis was conducted by *Scanning Electron Microscopy*,SEM analysis (FEI Type INSPECT-s50). The optical properties were analyzed through UV-Vis reflectance spectrum using spectrometer HR 4000 CG-
UV-Vis-NIR Ocean Optics.

The photocatalytic degradation on Methyl orange was conducted by applying nano TiO_2 powder and nano TiO_2-CA(NDC). The degradation used UV light at various times of 0, 10, 20,30, 40 and 50 minutes. The UV light was analyzed the spectrum range through UV Vis spectrometer scanning. In addition, a standard curve of methyl orange solution was prepared by measure the absorbance of various methyl orange concentrations. The standard curve was used to provideaconcentration of methyl orange based on its absorbance value after degradation. 10 mL of methyl orange solution(15 mg/L) was soaked with 0.167 g of the prepared photocatalyst and was illuminated by UV light which was set up at 12 cm distance from the methyl orange solution.The experimental setup is described in Figure 1. The same method also carried out by using the nano-TiO_2-CA(NDC) sheet. Each degradation test was conducted twice. Standard deviation of rate constant was drawn from the values calculated from those duplet data.

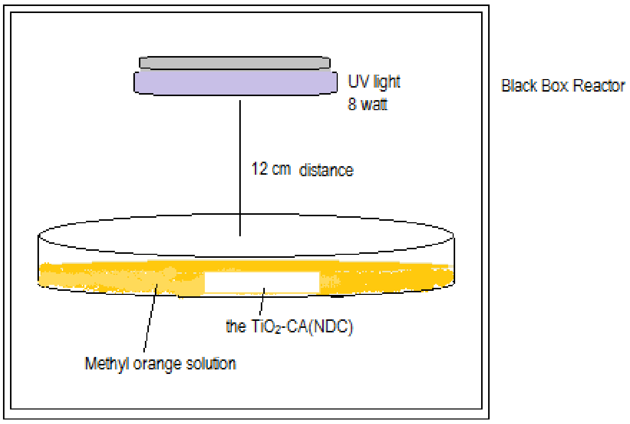


Figure 1. The experimental setup of Methyl Orange degradation

3. **Results and discussion**

3.1 The reaction to form cellulose acetate

The reaction between cellulose with anhydrous acetate produced cellulose triacetate and acetic acid as it is listed in equation(1). The reaction is called as acetylation. Meanwhile, during hydrolisis reaction, the cellulose triacetic react with water molecules to form cellulose diacetic and acetic acid. The formation of cellulose acetate was analyzed by FT-IR and produce spectrum depicted in Figure 2. The FT-IR spectrum of cellulose acetate is compared to the initial material, i.e. nata de coco. The FT-IR spectrum in Figure 2(a) shows a characteristic broad peak of OH streching at wavenumber 3485.52 cm^{-1}. It indicates the presence of hydrogen bonding between hydroxyl group in the cellulose network and also the surface OH groups. A peak of C-Ostretching present at 1052.21 cm^{-1}. Meanwhile, the produced cellulose acetate spectrum (Figure 2(b)) provides a new peak at 1751.44 cm^{-1} which are indicated as acarbonyl group, C=O stretching, and a sharp peak at 1240.28 cm^{-1} indicating the presence of acetyl C-O. The presence of acetyl C-O indicates that the OH group in cellulose molecules has been substituted by =CO group producing the cellulose acetate.

$$(C_6H_{10}O_5)_n + 3CH_3COOCOCH_3 \overset{H^+}{\leftrightarrow} [C_6H_7O_2(OOCCH_3)_3]_n + 3CH_3COOH \quad (1)$$

Cellulose   anhydrous acetate   cellulose triacetate   acetic acid

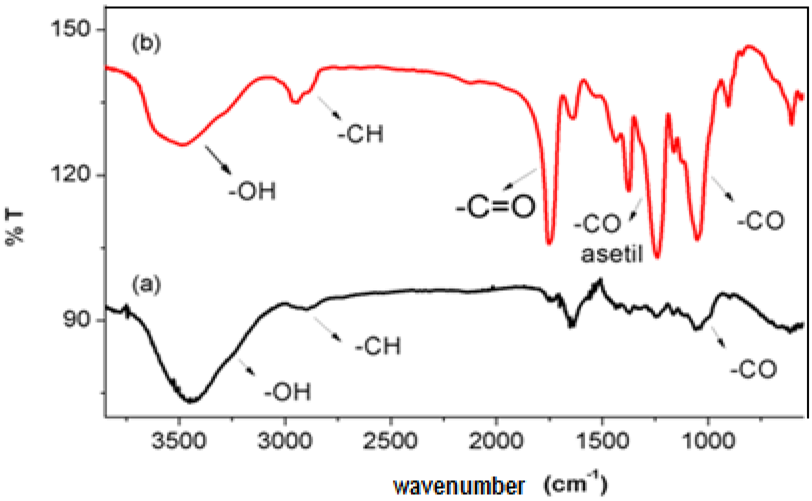


Figure 2. FT-IR spectrum of Nata de Coco (NDC) (a) and the prepared cellulose acetate (b).

Morphological analysis of the prepared nano TiO_2 with SEM analysis resulted in SEM images as described in Figure 3. The particle size which was estimated by MeasureIT program (the free edition) shows that the average diameter of the initial anatase TiO_2 is 207.39 nm ± 19.73. The initial TiO_2 was procured as anatase TiO_2 (98%, Japan). Meanwhile, the average diameter of the prepared nano-TiO_2 is 88.63 nm ± 4.37. The result shows that the destruction process with sodium hydroxide successfully reduced the particle size into nanosize particles. It is in agreement with the previous research by Rajabzadeh et al.[24].It also proves that the alkaline destruction might become an alternative way instead of other processes such as the hydrothermal method [25]. The alkaline destruction shows many advantages i.e. it is not expensive, no requirements on a specific equipment and high temperature. During destruction process, The Ti-O-Ti bonding was broken to form the Ti-O-Na and Ti-O-OH. The new Ti-O-Ti bondings were then formed during calcination at 450 ^oC [26].

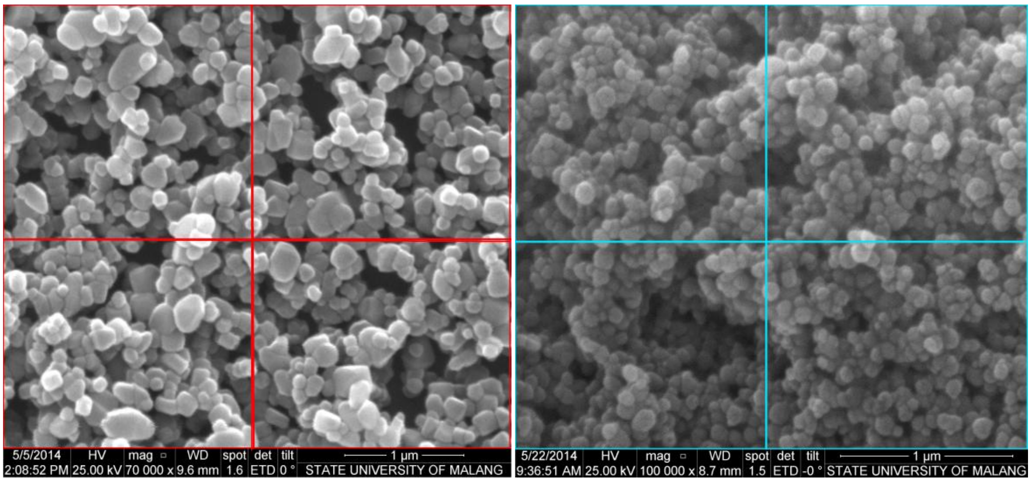


Figure 3. SEM images of the initial TiO_2 (A) and the TiO_2 after destruction process (B)

Image of the prepared nano TiO_2-CA(NDC) is described in Figure 4(a). The membrane has a white color, shiny and rigid. The thickness is 43.7 µm with porous surface morphology as described in Figure 4(b and c). The previous result withthesame method of preparation found the membrane thickness of 42.9 µm, also with the porous surface [17].

X –ray diffraction patterns in Figure 5 shows the change of TiO_2peaks, in which the peaks are sharp at initial to become broaden after destruction process with NaOH. The broad peaks represent small particle size and the material became amorphous. In the nano-TiO_2 diffraction pattern there are new peaks at 2θ of 31.825^o and 45.63^o which are identified as NaCl, as it was confirmed with standard diffraction of NaCl ICSD # 18189. The peak of NaCl also found in the previous research [17], as the reaction product between the remained sodium ions with chlorine ions during acid washing. The main peak of anatase TiO_2stillexists at 25.37 ^{o}, which is in agreement with standard diffraction of anatase TiO_2 ICDS #24276. It indicates that the destruction process did not change the phase of TiO_2 but it decreased the particle size and the crystallinity which was shown by broad peaks. The high peaks at 2θ less than 25^o refer to cellulose acetate, as it were confirmed by standard diffraction of cellulose acetate JCPDS#03-0021.Elemental analysis by EDX (Figure 6) shows that a 12.21 % of Ti are present in the prepared composite.

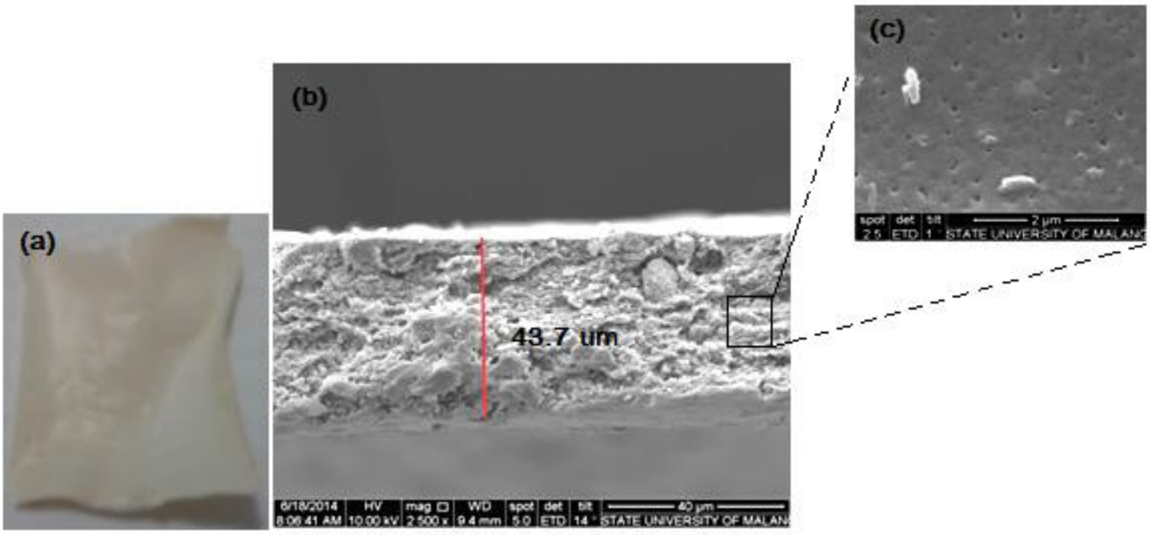


Figure 4. The images of membranenano TiO_2-CA(NDC) (a) the cross section SEM image (b)and its porous surface morphology

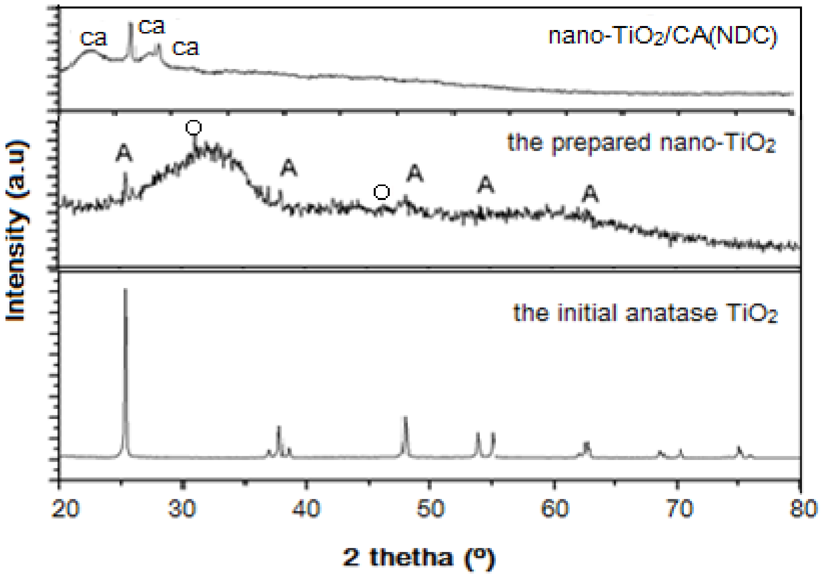
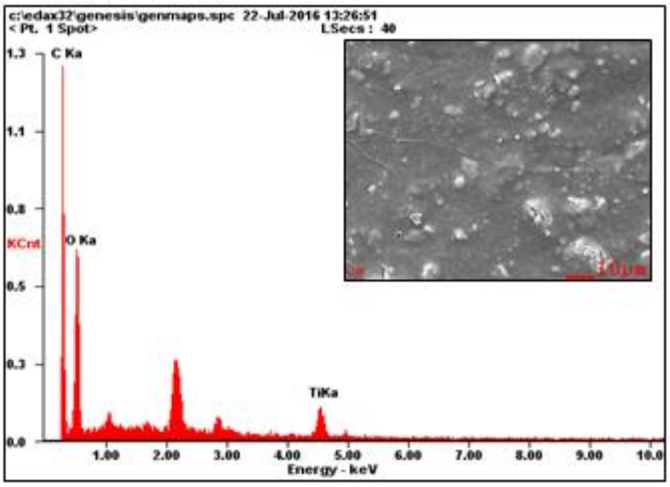


Figure 5. The diffraction pattern of the initial anatase TiO_2, the prepared nano TiO_2 and the prepared composite of nano TiO_2-CA(NDC). The sign o refers to the characteristic peak of NaCl.



Element	Wt%	At%
CK	44.68	55.78
OK	43.11	40.40
TiK	12.21	03.82

Figure 6. EDX analysis of TiO_2/CA

3.2 The photocatalytic performance of materials on methy orange solution

The maximum wavelength absorbance of methyl orange solution was found at 464.27 nm, which was in agreement with Ramadhana [27] who found at 464 nm. This maximum wavelength absorbance was used to analyze methyl orange concentration after degradation. Meanwhile, The UV lamp used as a light source has 8 watts of power, and the absorbance pattern (Figure 7) shows that the UV lamp is not a monochromatic lamp. The active wavelength is between 313.39 – 412.95 nmwith a maximum absorbance at 370.91 nm. Therefore, the UV light source used can be defined to haveawavelengthof 370.91 ± 25.01 nm. The wavelength is shorter than the wavelength of light that comparable to the band gap energy, E_g, of TiO_2 i.e. 380 nm (comparable to 3.2 eV). It means that the energy of UV lamp capable to excites the electrons, *e*-, fromthevalence band to the conduction band and producingahole, h^+, at the valence band. The holes will react with H_2O to produce hydroxy radicals [28]. The degradation reaction is proposed in equation (1), (2), and (3).

$$TiO_2 + hv \longrightarrow hole^+ + e^- \quad (1)$$

$$H_2O + hole^+ \longrightarrow OH\bullet + H^+ \quad (2)$$

$$OH\bullet + \textit{methyl orange} \longrightarrow \text{product (simpler molecules than Methyl Orange)} \quad (3)$$

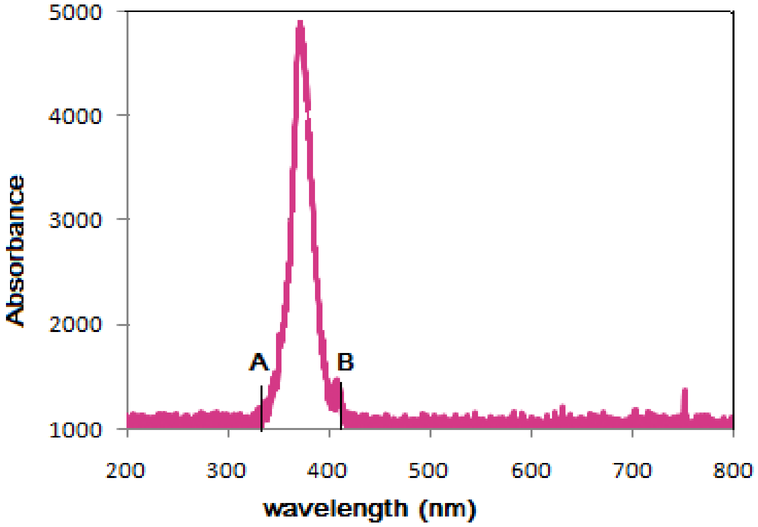


Figure 7. The UV Vis absorbance of UV light. A is 313.39 nm, B is 412.95 nm, and the highest absorbance is at 370.91 nm. The UV lamp power is 8 watts.

Kinetics plots of methyl orange degradation (Figure 8 and 9) show that the photocatalytic degradation with nano-TiO_2 and TiO_2-CA(NDC) able to decrease methyl orange concentration. Meanwhile, the adsorption and photolysis method provided anonly small decrease in methyl orange concentration. It indicates that the TiO_2-CA(NDC) only has low adsorption capability, with arate constant of 0.0013 $ppm.min^{-1}$. Meanwhile, the UV radiation without the present of photocatalyst also only reduce the methyl orange concentration at a rate constant of 0.0009 $ppm.min^{-1}$.The photodegradation using nano-TiO_2 and TiO_2-CA(NDC) have higher linear regression constant, R^2, at second order kinetics than the first order kinetics, indicates that the photodegradation prefers to follow second order kinetics.The result is different with the other result on methyl orange degradation with TiO_2 P25 Degussa asaphotocatalyst that follows first order [29]. It is probably because of the dynamics of reaction that varies depent on the reaction system. Beside of the fact that photocatalytic process are very complex, and some aspect of the reaction mechanism and reaction kinetics are unclear [30]

This research found that the rate constant of degradation using nano-TiO_2-CA(NDC) is 0.01±0.002 $ppm.min^{-1}$. The value is lower than the rate constant of degradation using nano-TiO_2 powder asacatalyst, i.e. 0.015±0.003 $ppm.min^{-1}$. The rate constant valueof degradation with nano-TiO_2 powder is actually higher than the degradation of methyl orange solution with a composite of TiO_2-zeolite, in which the rate constant value is 0.009 $ppm.min^{-1}$[27].However, after the nano-TiO_2 is embedded in a CA membrane, the rate constant value decrease and it is comparable tothe degradation using TiO_2-zeolite. The rate constant value shows that the immobilization of nano-TiO_2 into CA(NDC) decrease the photocatalytic activity of the catalyst. The CA membrane itself might inhibites the radiation of UV light to TiO_2 molecules. When the data was analyzed by statistical method i.e. the T analysis, it is known that the different on the rate constant values are not significant. It means that in the point of view of statistical analysis, the photocatalytic activity of the nano-TiO_2 powder and its immobilized form in CA(NDC) membrane is similar. However, the immobilized form offers the advantage on eliminating the separation process from the treated solution. It will reduce a significant large cost when it is applied to a large scale. A half time of degradation, $t^{1/2}$, that representthetime required to degrade the half number of methyl orange molecules is also calculated by applying equation (5) :

$$t^{1/2}{}_{2\text{-order}} = \frac{1}{k[A]o} \qquad (5)$$

$[A]_o$ is the initial absorbance of the treated solution. It means that the initial concentration affects the half time parameter. High concentration will lead to a smaller value $t^{1/2}$. Calculation found that the $t^{1/2}$ is 77 minutes when the degradation used nano-TiO_2 powder as acatalyst, and the $t^{1/2}$ is 115 minutes when the nano-TiO_2 is immobilized into CA(NDC). However, the half time will reduce significantly when the composite nano-TiO_2-CA(NDC) is used to degrade a high concentrate of methyl orange.

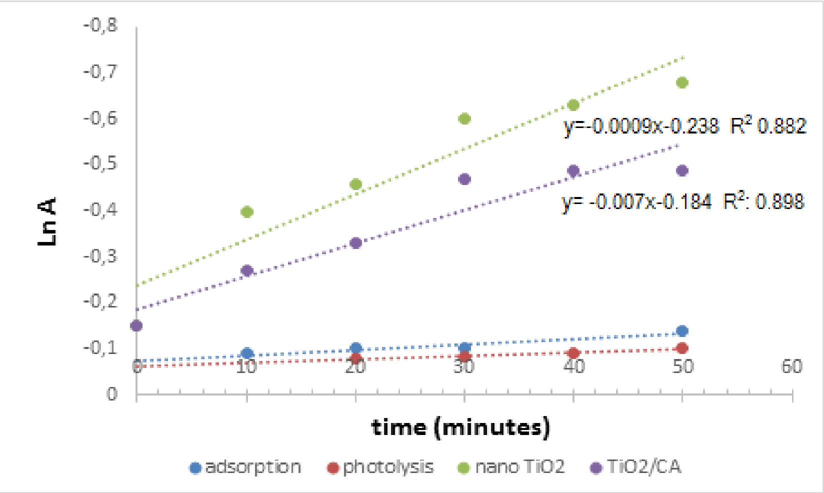


Figure 8. First order kinetics plots of methyl orange photodegradation with nano-TiO_2 powder and TiO_2-CA(NDC) in comparison with the adsorption performance of TiO_2-CA(NDC) and the photolysis under UV irradiation.

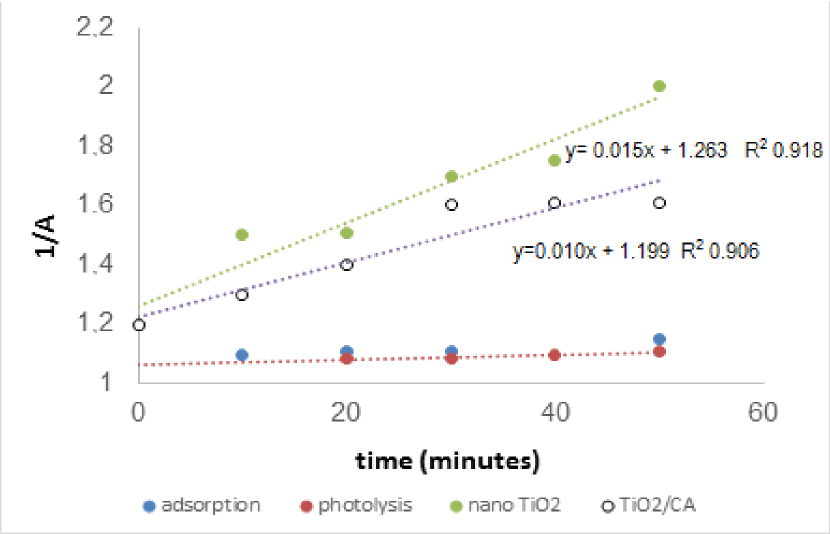
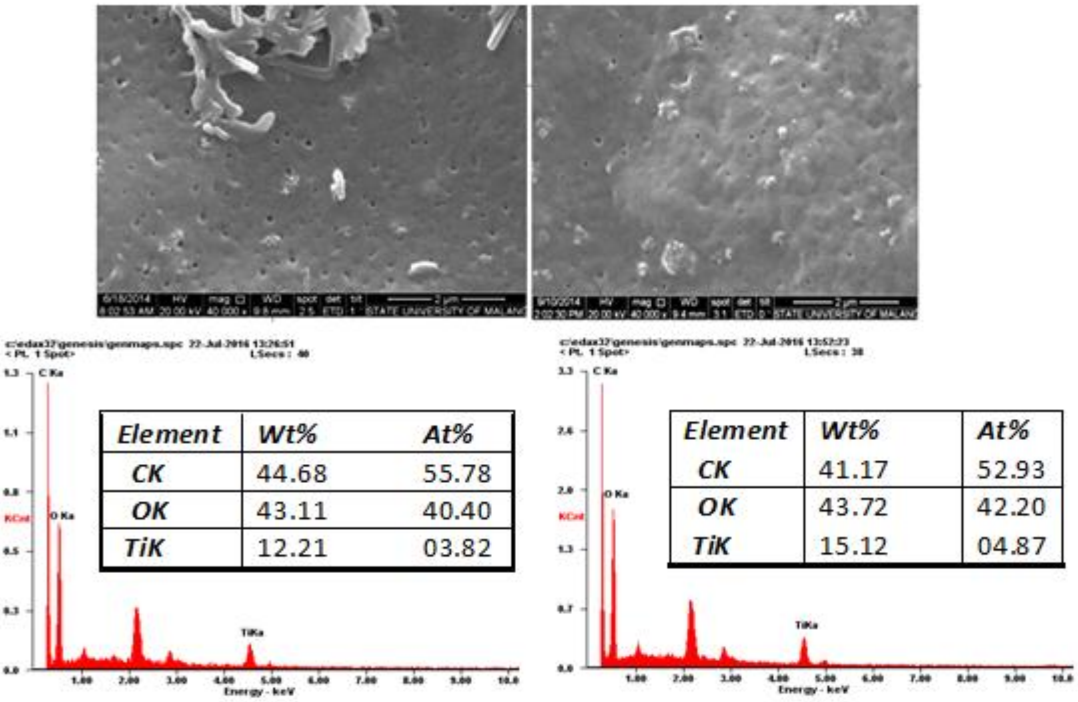


Figure9. Kinetics of the second order of methyl orange photodegradation with nano-TiO_2 as photocatalyst and nano-TiO_2-CA(NDC) as aphotocatalyst, in comparison with the adsorption performance of TiO_2-CA(NDC) and the photolysis under UV light irradiation.

This research also analyzes the change in surface morphology after degradation, as described in Figure 10. At initial, the surface morphology of nano-TiO_2-CA(NDC) is not homogeneus by presenting a coral like a form of CA membrane (Figure 10(a)). After being used for methyl orange degradation, the surface morphology change to become more homogeneus than the initial morphology, as described in Figure 10(b). It indicates that during degradation process, the energy of UV light also capable ofdegrading the cellulose acetate molecules in the host membrane. It also means that this composite photocatalyst has a limited life on applications. The EDX analysis on the photocatalyst at before and after degradation also show the change in composition, especially the decrease of C content. It indicates that cellulose might undergo self degradation during photocatalytic process. An investigation on this cellulose degradation will be interesting to understand the cycling ability of the TiO_2-CA(NDC) in terms of its substrate stability. Meanwhile, the EDX analysis shows that TiO_2, the photo-active material is fully recovered by the membrane or the substrate.



Element	Wt%	At%
CK	44.68	55.78
OK	43.11	40.40
TiK	12.21	03.82

Element	Wt%	At%
CK	41.17	52.93
OK	43.72	42.20
TiK	15.12	04.87

Figure10. SEM images of membrane before and after degradation and the EDX result of membrane at before (a) and after degradation (b)

Conclusions

The immobilized nano-TiO_2 in a cellulose acetate (CA) from nata de coco (NDC) show a photocatalytic activity on methyl orange degradation with the rate constant of 0.01±0.002 ppm.min^{-1}. Eventhough, the rate constant value is lower than the methyl orange degradation with nano-TiO_2 powder, however, the immobilized form offers an advantage of separation process from the treated solution. Statistical analysis also found that the difference in the rate constant is not siginificant. It means that the immobilization of nano-TiO_2 into a CA(NDC) membrane will not reduce the photocatalytic activity of TiO_2. The positive impact is it will reduce the application cost due totheelimination of separation treatment.

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References

1. Znaidi L., Seraphimova R., Bocqouet J.F., Colbeau-Justin C., Pommier C., *Mat.Res. Bull.* 36 (2001) 811-825.
2. Christina M., Mu'nisatun S., Saptaji R., Marjanto D., *Jurnal Forum Nuklir.* 1 (2007) 31-44.
3. Sopyan I., Mitsuru W., Sadao M., *Chem. Lett.* (1996) 69-70.
4. Xu N., Sui Z., Yigun F., *Ing. Eng. Chem. Re.s*, 38 (1999) 375-379.
5. Rajh T., *J. Phys. Chem.* 100 (1996)4538-4545.
6. Chen Y., Xiong X-P., Yang G., Zhang L-N., Lei, S-L., Liang H., *Chinese J. Polym. Sci.* 20 (2002) 369-37
7. Kolar M., Ankova H.M., Jirkovsky J., Heyrovsky M., Subrt J. *Langmuir*. 22(2006) 598.
8. Lee S.H., Kang M., Cho S.M., Han G.Y., Kim B.Y., Yon K.J., Chung C.H., *J. Photochem. Photobiol. A: Chem.* 146(2001)121-128.
9. Rahmawati F., Kusumaningsih T., Hapsari A.M., Hastuti A., *Chem. Paps.*64(5) (2010)557-565.
10. Huang C-W, Liao C-H, Wu J.C.S., *J. of Clean En. Tech.*1(1) (2013)1-5.
11. Park J.H., Kim S., Bard A.J. *Nano Letters.* 6(1)(2006)24-28.
12. Wittmar A., Thierfeld H., K¨ochera S., Ulbricht M., *RSC Adv*. 5 (2015) 35866–35873.
13. Zularisam A.W., Ismaila A.F., Salimc M.R., Sakinaha M., Ozakid H., *Desalination,* 212 (2007) 191-208.
14. Zhou W., He J., Cui S., Gao W., *The Open. Mat. Sci. J.* 5 (2011) 51-55.
15. Abedini R., Mousavi S.M., Aminzadeh R., *Desalination* 277(2011)40-45
16. Aminzadeh R., Mousavi S.M., Abedini R., *Chem. Indust. Chem. Eng. Quart.* 18(2012) 385-398.
17. Ernia R., Mudjijono, Saraswati T., *Alchemy*. 11(2015) 90-101.
18. Natalia V. *Karakterisasi* TiO_2 *struktur nano pada selulosa asetate nata de coco. Thesis.* Universitas Sebelas Maret.(2013).
19. Radiman C.L., Yuliani G., *Polym. Int.* 57(2008) 502-508.
20. Desiyarni, *Perancangan proses pembuatan selulosa asetat dari sellulosa mikrobial untuk membrane ultrafiltrasi, Thesis,* Institut Pertanian Bogor (2006).
21. Bhongsuwan D., Bhongsuwan T., *Kasetsart. J. (Nat.Sci.).* 42(2008) 311-317.
22. Bydson J.A. *Plastic Materials*, London, Butterworth-Heinemann (1995)
23. Kuo C.M., Bogan R.T., *Process for the manufacture of cellulose acetate*, US Patent. 5(1997) 1-8.
24. Rajabzadeh G.H., Firuzian A., Hamzelahdeh P., *Polym. Int.* 57 (2008) 502-508.
25. Sikhwivhilu L.M., Mpelane S., Moloto N. Ray S.S., *Council Sci. Indust. Res.* 3 (2010)1-5.
26. Cui L., Hui K.N., Hui K.S., Lee S.K., Zhou W., Wan Z.P., Ha-Thuc C.N., *Materials Letters*, 75 (2012) 175-178.
27. Ramadhana, Al Kautsar K., Wardhani S., Purwonugroho D., *Student J.* 1 (2013) 168-174.
28. Hoffmann M.R., Martin S.T., Choi W., Bahnaman D.W., *Chem. Rev.* 95 (1995) 69-96.
29. Rashed M.N., El-Amin A.A. *Int. J. of Phys. Sci.* 2(2007)073-081.
30. Yan L., Cheng Y., Yuan S., Yan X., Hu X., Oh K., *Res Chem Intermed.* 39 (2013) 1673-1684

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