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Development of Material Nanocellulose/TiO_2 Composites for Photocatalytic Degradation of Paracetamol in Aqueous Medium

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Abstract: **-** Development of material nanocellulose/TiO_2 composites for photocatalytic degradation of paracetamol in aqueous medium has been studied. Raw material for the synthesis of nanocellulose (NC) was empty palm oil bunches (EPOB). The effects of TiO_2 loading on the synthesis of NC/TiO_2 composites (NCT) as photocatalyst and the photocatalyst concentration on photodegradation of paracetamol were carefully examined. The rod-shaped nanocellulose structures was obtained based on TEM analysis. Additionally, nanocellulose has been successfully composited with TiO_2, as corroborated XRD and FTIR analysis. The composite sample with TiO_2 loading of 70% on nanocellulose (30% NC/TiO_2) via sonication method evidently was outperformed other samples in photodegraded solutions containing 15 ppm of paracetamol, 2 g/L of photocatalyst for 4 hours until it meets the lowest concentration (1.43 ppm).

Keywords: nanocellulose, TiO_2, photodegradation, paracetamol.

I. INTRODUCTION

In the last decade, the field of nanotechnology for advanced materials has been extensively studied. TiO_2 is a semiconductor that has many applications (1) and is photocatalyst which has many advantages such as non-toxic, stable, not harmful, inexpensive and has hydrophilic properties (2,3). The application of TiO_2 includes as photocatalyst in H_2 production (4,5), pollutant degradation, self-cleaning, and for purification air and water (1), antimicrobial (6) and even for cancer therapy (2). This process involving electrons (e-), holes (h+) and hydroxyl radicals resulting from the photocatalytic process. This radical is the most reactive and effective substance in oxidizing pollutants and kills microbes by damaging the cell walls. But in its application, this material has low efficiency and separation problems after use. Therefore, supporting materials such as zeolite, silica, graphene, pumice and others are needed so that it can increase efficiency in its application.

On the other hand, nanocellulose (organic polymer) is also in great demand and gets attention as a buffer/adsorbent in waste degradation and antibacterial applications due to its physical (unique structure), chemical and biological properties (7). This material is very compatible, stable and environmentally friendly. Nanocellulose can be obtained from insulating materials such as straw, empty oil palm bunches, oil palm trunks, hemp and fiber. At the moment, nanocomposite materials from inorganic nanoparticles (TiO_2) and organic polymers (nanocellulose) has received great attention because it produces a superior material due to synergistic effect of the interaction of the constituent materials (8,9). This material can be used for degrading pollutants (1,9,10), antimicrobial applications, self-cleaning materials (1,7), and membrane filtration (11,12). Currently, nanocomposites which combining polymers and materials inorganic have unique properties compared to the polymeric membranes that are made conventionally. In addition, the application of TiO_2 which is composited with nanocellulose has shown improvement of TiO_2 properties such as having good stabilization, enhancing photocatalytic, antibacterial, hydrophilic and anti-fouling properties (9). Nanocellulose, a porous material, is a good candidate as TiO_2 buffer material and adsorbents. Photocatalytic degradation of waste with TiO_2 coatings on other materials have been studied and applied such as silica/TiO_2, zeolite/TiO_2, graphene/TiO_2, pumice/TiO_2 and carbon nanotubes/TiO_2 (10). But so far, the use of nanocellulose/TiO_2 based nanocomposites for photodegradation hospital waste containing paracetamol is rarely studied.

In recent decade, there is a raising a new problem namely increasing amount of hospital waste generated. Hospital wastewater contains high organic components (microbes, antibiotic residues and other organic components) and inorganic (nitrates, phosphates, chlorides, etc.). These wastes must be treated properly so it is not polluting the environment. Several methods been used to treat hospital waste such as ozonation, chlorination, UV radiation, flocculation, anaerobic and aerobic, and membrane technology (13). Meanwhile, photocatalysis with TiO_2 is also one of the most promising effective waste treatment methods (10,14). Nanocomposites consisting of inorganic nanoparticles such as TiO_2 and organic polymers such as cellulose have been studied by previous researchers with

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the sol gel and inversion method for phenol degradation (12), ultrasonic method for acid methanamics degradation (10), and blending methods for ultrafiltration (5). Modify nanocellulose with TiO_2 was carried out because nanocellulose could be used as a buffer material which can increase the surface area of TiO_2 and can also enhance distribution and transfer TiO_2 surface electrons. Thus, this nanocomposite synergistically can be a material to degrade waste and antimicrobial more effectively. The development of nanocellulose/TiO_2 composites is an effort to treat waste to create zero waste conditions. Besides, the source of nanocellulose that will be used is extracted from OPEFB waste produced from numerous oil palm plantation activities. In 2022, production OPEFB waste in Indonesia is 51 million tons/year (15) with a cellulose content of 37.3 – 46.5% (16).

To the best of our knowledge, development of nanocellulose/TiO_2 composites for photocatalytic degradation of paracetamol in aqueous medium has not been studied in detail. Therefore, we study and examine the effect of TiO_2 loading on the synthesis of nanocellulose/TiO_2 (NCT) composites as photocatalyst and the photocatalyst dosage (loading concentration) on photodegradation of paracetamol.

II. Materials and Methods

2.1. Materials

Empty palm oil bunches (EPOB) was collected from palm oil factory in Kalimantan. Analytical grade of acetone/C_3H_6O (80%), NaOH, acetic acid/CH_3COOH (100%), $NaClO_2$ (80-83%), and H_2SO_4(95-98%) were supplied by Merck or Sigma Aldrich. These all chemical were used without further purification. TiO_2-P25 (79% anatase, 21% rutile) with the crystalline size of 20 and 23 nm was procured from Evonic Industry.

2.2. Extraction of nanoellulose

To extract nanoellulose, EPOB was soaked for 1 day, followed by washig with distilled water and acetone to clean the dirt and dried at 60°C in oven. Size reduction of EPOB was performed using Fomac FGDZ 500, and then it was sieved at 100 mesh. The next process is alkalization with NaOH 4 wt% at 80°C for 3 hours of the dried sample. The next steps were washing the sample until pH reached 7 (neutral), bleaching with acetate buffer solution (a mixture of distilled water, NaOH, acetic acid) under stirring at 80°C for 2 hours, and neutralizing the solution to pH 7. Subsequently, the solution was bleached with $NaClO_2$ at 80 C for 2 hours and neutralized. The alkalization with NaOH aims to remove hemicelluloses and lignin from the solution. Meanwhile, bleaching process is done to break down the phenolic compounds present in lignin and also to remove by-products from the solution.

To synthesize the cellulose from EPOB, drying the bleached product and hydrolysis with H_2SO_4 30 wt% at 40 °C for 45 minutes was performed and followed by cooling to stop the reaction. To remove excess H_2SO_4 and water-soluble materials, centrifugation 6000 rpm at 10 °C for 10 minutes was performed followed by sonication for 40 minutes and finally the product is dried by freezing. To remove the amorphous part of the extracted cellulose, the hydrolysis was performed therefore cellulose nanocrystals was produced. Meanwhile, dialysis and sonication process aims to remove any free acid molecules and to disperse nanocellulose crystals.

2.3. Preparation of NC/TiO2 composites (NCT)

Nanocellulose (NC) was synthesized from EPOB with acid hydrolysis using H_2SO_4 50%. Sonication method was developed for synthesis of composites of NC/TiO_2. About 30, 50, 70, and 100 (wt%) of NC and 70, 50, 30 and 0 (wt%) of TiO_2 with total weigh of 1 gram was added to 100 ml of acetone and followed by sonication in an ultrasonic batch for 1 hour by maintaining a temperature of around 40°C. The composite is denoted as NC/TiO_2. The solution was then dried at 70°C in the oven for 2-3 hours until the remaining solution was 50 ml and stored in seal glass vials.

2.4. Photodegradation experiment

The photocatalytic performance of NC/TiO_2 was performed for paracetamol photo degradation with UV light irradiation with 12 mercury lamp @ 8 watt (total = 96 watt) placed on top of the photoreactor. Both adsorption and photodegradation were performed in a 2000mL glass photoreactor under continuous stirring at room temperature (30-36°C). The temperature was maintained by installing an exhaust fan on the side of the photoreactor.

Adsorption tests were conducted in darkness for 1 hour before photodegradation begins to determine the contribution of adsorption to the total removal rate of paracetamol. After the adsorption equilibrium, photocatalytic degradation was performed by illuminating solutions of paracetamol with certain amount of NC/TiO_2 composite with UV lamp. A magnetic stirrer was used for homogenizing of NC/TiO_2 and paracetamol solution in the photoreactor. All tests utilized 2g/L of NC/TiO_2 in concentrations of paracetamol around 15 ppm for 4 hours degradation. Every hour, an aliquot of 5mL solution sample was taken to measure the paracetamol concentration. The absorbances of the solution were recorded using double beam spectrophotometer (Shimadzu UV-1700, Japan) at 243 nm. All experiments were performed in duplicate.

III. Characterizations

Extracted nanocelllose and the synthesized composite were subjected to various characterizations for obtaining functional groups, phases and morphology using Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffractometer (XRD) and transmission electron microscopy (TEM) characterization for the NC.

3.1. XRD analysis

To determine the crystalline nature of TiO_2, nano cellulose produced and the composite, X-ray diffractometer (XRD) (Bruker, BRIN) using Co Kλ (Kλ = 1.78897 A˚) as a radiation source over the 2θ range (degrees) of 10–120º was used and generated at 40 kV and 30 mA.

3.2. FTIR spectral analysis

Fourier Transform Infrared Spectroscopy (FTIR Thermo Scientific Nicolet iS50 + NIR Spectrometer owned by Universitas Indonesia) characterization was performed to examine the changes in functional groups of samples (TiO_2, NC dan composite NC/TiO_2). FTIR measurements were performed at wavenumber between 400–4000 cm^{-1}.

3.3. TEM analysis

TEM (Tecnai G2 SuperTwin TEM/STEM) analysis was used to examine the morphology and nanosized of NC

IV. RESULTS AND DISCUSSION

4.1. XRD analysis

Figure 1 presents XRD spectra of synthesized NC, pure TiO_2 and NC/TiO_2 composite. In the case of NC, the pattern shows broad peaks 22.5˚ represent the typical cellulose I structure (10) as presented in Figure 1(a). The peak intensity at a 2θ value of 25.3º and 27.4º related to their crystalline phases of of anatase and rutile of TiO_2 as shown in Figure 1(c) (10). Meanwhile, the NC/TiO_2 composite showed XRD patterns similar to those of the two precursors (NC and TiO_2) as shown in Figure 1(b). XRD analysis results show that the NC/TiO_2 composite has been formed.

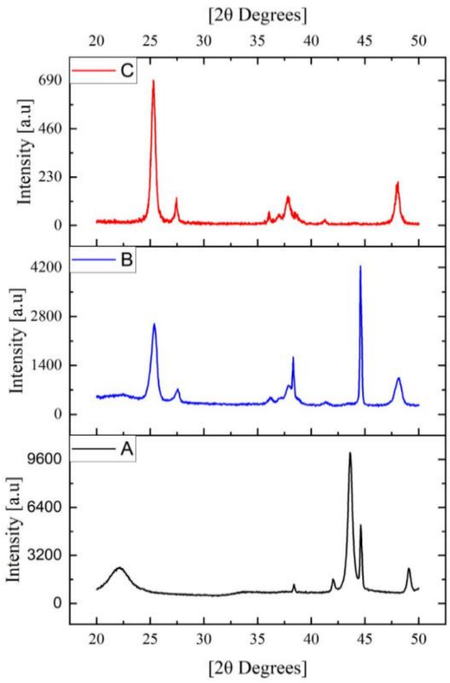

Figure 1. XRD spectra of (a) NC, (b) NC/TiO_2, and (c) TiO_2

4.2. FTIR analysis

The FTIR spectra for NC, TiO_2 and NC/TiO_2 composite were recorded over the wave number range between 500-4000 cm^{-1} as presented in Figure 2. A strong and weak band at 3000-3400 cm^{-1} were observed in all materials were attributed to surface OH group peaks (10). The band at around 2870 cm^{-1} corresponds to C-H stretching groups which present in NC and NC/TiO_2 composite (17,18). The spectra at around 1634 cm^{-1} presents in NC represent aromatic C=C group. The peak at 970 cm^{-1} was observed in NC and NC/TiO_2 representing C-H rocking vibration of cellulose present in the microfibers and nanofibers (10). The peak around 750 cm^{-1} correspond to TiO_2 (19). At the wave number 1900 -2200 cm^{-1}, there is a peak which is the absorption from the ATR diamond and the detector in the FTIR equipment.

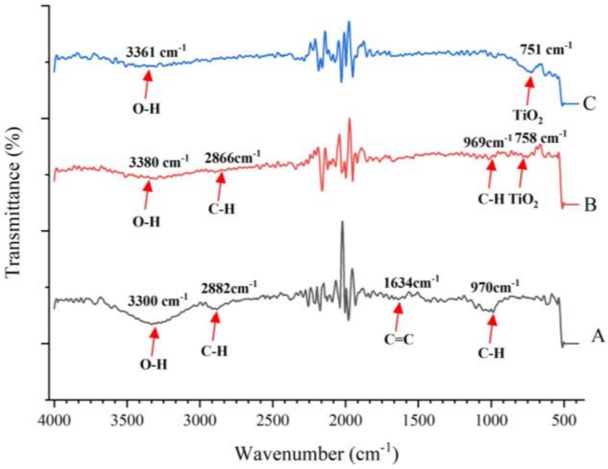

Figure 2. FTIR spectra of (a) NC, (b), NC/TiO_2 and (c) TiO_2

4.3. Photocatalyic study.

The effects of the amount of photocatalyst on photodegradation is depicted in Figure 3 with the loading of 1g/L and 2g/L. Photodegradation with loading 2g/L of composite NC/TiO_2 displayed more efficient for paracetamol degradation. When the loading of photocatalyst is increased, the accessibility of active site on the photocatalyst surface increases, resulting in the more formation of OH radicals, and therefore many photodegradation reactions occur.

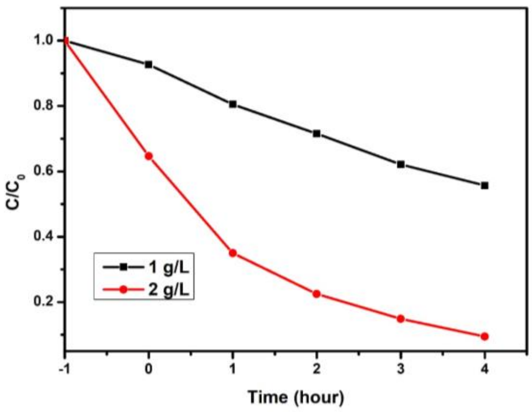

Figure 3. The effect of photocatalysts concentration on paracetamol degradation with initial concentration 15 ppm and composite 30%NC/TiO_2

The photocatalytic activity of NC/TiO_2 was conducted using initial paracetamol concentration of around 15 ppm and photocatalyst dosage of 2g/L as shown in Figure 4 with 0, 30, 50, 70 (wt%) of NC in the composite. The paracetamol concentration value is the average of duplicate data. In this process, in the first hour there is no UV light exposure. Therefore the photodegradation process had not occurred because there was no UV light irradiation, so the reduction in paracetamol concentration was due to the adsorption process. Figure 4 shows that in the first hour without UV irradiation, the more TiO_2 in the NC/TiO_2 composite, the greater the decrease in the paracetamol concentration. This shows that there is more adsorption of paracetamol by TiO_2 than adsorption by NC.

In the photodegradation process for 4 hours, there was a decrease in paracetamol concentration. Without any photocatalyst (only NC in the solution) and under UV light irradiation, paracetamol concentration displayed insignificant reduce (constant). This means there is no degradation and adsorption process of paracetamol by NC. Furthermore, the more TiO_2 in the composite, the greater the decrease in paracetamol concentration. Photocatalyst with doping 30 w% NC (70 w% TiO_2) displayed the highest photocatalytic activity. This is because the ability of NC to help capture electrons so that the recombination of electrons and holes resulting from the photocatalysis process can be reduced. Thus, many OH radicals react with paracetamol to become CO_2 and H_2O. Moreover, the photodegradation rates of NC/TiO_2 were in accordance with their adsorption capacities, which were proportional to the TiO_2 loading and the optimal performance was obtained with TiO_2 loading of 70 wt% in both photodegradation and adsorption. Furthermore, under these conditions the number of active sizes increases, which results in more effective interactions resulting in the formation of more OH radicals which attack paracetamol.

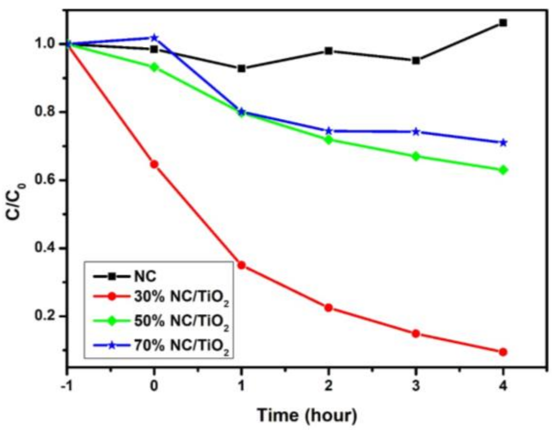

Figure 4. Photocatalytic activity of NC and NC/TiO_2 with composite concentration 2 g/L at various loading TiO_2 on NC.

V. CONCLUSION

Development of material nanocellulose/TiO_2 composites for photocatalytic degradation of paracetamol in aqueous medium has been studied. Cellulose was successfully extracted from OPEB using chemical treatments (alkalinization, bleaching and followed by hydrolysis processes). Nano size of cellulose produced has the average diameter 1.66 and length of 9.85 nm with rod-like shape based on TEM characterization. This nanocellulose/NC is then composited with TiO_2 to form NC/TiO_2 nanocomposites which are used for photodegradation of waste containing paracetamol 15 ppm with optimal conditions at a concentration of 2g/L. Optimal process conditions were achieved at TiO_2 loading of 70 (w%) in nanocellulose and this composite was able to degrade waste up to 90% removal.

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