The Effect of TiO_2 Loading on Nanocellulose (NC)/TiO_2 Solid Composite and pH on Paracetamol Photodegradation

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ABSTRACT
These days, organic contaminants from the pharmaceutical industry are a constant global issue that pollute water supplies. This study examined the effects of pH on the photodegradation of paracetamol and TiO_2 loading on the synthesis of NC/TiO_2 solid composites (NCT) as a photocatalyst. Low concentration of acid is used on hydrolysis to extract nanocellulose from empty palm oil bunches (EPOB), and SEM analysis shows that the impregnation approach produced NCT effectively. The optimal conditions for photodegradation of waste containing 15 ppm paracetamol with a concentration reduction of up to 60% for 4 hours are provided by NCT with TiO_2 loading of 70% on nanocellulose (NCT 30-70) as much as 1 g/L at pH 6. Reusing photocatalyst demonstrates a 13% reduction in photocatalyst ability up to 4 cycles.

1. Introduction:

The surge in pharmaceutical waste production is one of the new issues that have emerged in the past ten years due to population growth and the onset of several ailments. High concentrations of organic materials, including paracetamol, are present in this trash, which needs to be treated carefully to prevent environmental contamination. One medication that lowers temperature and pain is paracetamol. Pharmaceutical waste containing paracetamol has been treated using a variety of techniques, including membrane technology, flocculation, ozonation, and chlorination [1]. In the meantime, TiO_2-based photocatalysis technology is another potential waste-processing technique [2], [3], [4]. Therefore, environmental protection can be performed by controlling organic pollutants in water sources.

TiO_2 is an inorganic semiconductor with a wide range of useful applications and a photocatalyst that offers several benefits because it is inexpensive and non-toxic [5], [6]. Since TiO_2 is a semiconductor with a broad band-gap, high surface area, and good stability, it is a good material for photocatalysis [5]. TiO_2 can be used as an antibacterial agent [6] and as a photocatalyst in the creation of hydrogen and the breakdown of pollutants [4], [7]. When the material is exposed to photons with energy equivalent to or higher than the TiO_2 energy band gap, electrons in the valence band (VB) are excited to the conduction band (CB), leaving holes in the VB. The redox reaction of adsorbed species will be started when electrons and holes migrate to the surface of TiO2. The photo-generated holes will oxidize water to produce •OH (hydroxyl radical), meanwhile the photo-generated electrons will undergo a reduction reaction with oxygen to produce •OH. These radicals are the most reactive and effective substances in degrading pollutants [5]. The mechanism of photocatalytic process could be explained according to the reaction as follows [8]:

$$\text{Organic pollutants} + \bullet OH \rightarrow CO_2 + H_2O \text{ (decomposed products)} \quad (1)$$

TiO2 nanoparticles tend to agglomerate, lose some of their useful surface area, and are incapable of recovering, which poses serious challenges to their applications [9]. Nevertheless, this material has separation issues after use [2]. The high electron-hole recombination rate is another drawback; as a result, supporting materials are needed to deposit TiO_2 and create composites. Supporting materials have the ability to reduce electron-hole recombination by acting as an electron trap. Because of the synergistic effect of the constituent elements' interaction, nanocomposites generate superior materials [5], [10], [11].

As was previously mentioned, immobilizing TiO_2 nanoparticles in an appropriate scaffold—such as cellulose generated from biomass—is an efficient way to deal with this problem. Straw, empty oil palm fruit bunches, oil palm stems, hemp, and fiber are a few examples of this biomass. The selected nanocellulose was cellulose nanocrystal (CNC), which is made up of rod-shaped cellulose crystals (length: 100–500 nm, width: 5–10 nm) that were created by acid hydrolyzing a pure cellulose source to remove its amorphous components [12]. Among CNC's unique characteristics are its large surface area, strong mechanical properties, and negatively charged sulphuric groups (apart from hydroxyl groups on the cellulose surface) [13]. In this context, cellulose may represent as ideal platform for creating hybrid organic-inorganic nanocomposites such as nanocellulose-TiO_2 (NCT) [5]. The NCT has been studied by previous researchers using sol-gel, ultrasonic methods, impregnation methods, mixing methods, and blending methods for ultrafiltration [2], [5], [6], [9].

Apart from that, the source of nanocellulose that will be used will be extracted from EPOB waste, which is generated by Indonesia's extensive oil palm plantation operations. To the best of our knowledge, no thorough study has been conducted on the development of nanocellulose/TiO_2 solid composites for photocatalytic degradation of paracetamol in aqueous medium. In our previous study, we synthesized and applicated the NCT in the liquid form [14]. Thus, we investigate and analyse how TiO_2 loading on NC nanocellulose (0, 30, 50, and 70% by weight) affects the photocatalytic performance of the resultant solid nanocomposites (NCT), pH (3, 6, and 9), and their reusability during the degradation process. Real hospital waste will be used to test the process's optimal outcomes. It is envisaged that this technology's success will help address the issue of environmental contamination.

2. Material And Methods

Material

Empty palm oil bunches (EPOB) from Kalimantan. NaOH, CH_3COOH (100%), $NaClO_2$ (80-83%), H_2SO_4 (95-98%) and acetone were supplied by Merk and Himedia. These all chemicals were used without purification. TiO_2-P25 (79% anatase, 21% rutile) was procured from Evonic Industry.

Extraction of Nanocellulose, Impregnation and Photodegradation

Nanocellulose (NC) is extracted from EPOB via alkalization with NaOH, bleaching with acetic acid and $NaClO_2$ followed by hydrolysis processes with H_2SO_4 according to procedures as mentioned in previous studies (12).

Impregnation of TiO_2 P-25 nanoparticles in nanocellulose (NC) was carried out by weighing nanocellulose dissolved in acetone and adding TiO_2 (variations of 0, 30, 50 and 70% by weight) with a total weight of 1 gram, stirring ultrasonically (14). It was dried using an oven to get nanocomposite NCT in the solid form. To determine the elemental composition and morphology of the solid NCT photocatalyst, characterization was carried out using SEM (Thermo Scientific - Phenom Pharos G1 SEM-FEG).

Photodegradation experiments were carried out in the photoreactor box illuminated with 96 W UV lamp as the photon source. One gram of NCT was added to the 1 L solution containing paracetamol with concentrations of 15 ppm. Then the percentage of degradation is measured every hour for 4 hours using a spectrophotometer (Shimadzu UV-1700, Japan) at a wavelength of 243 nm. The photodegradation is carried out at different pH of 3,6 and 9 adjusted by adding HCl or NaOH and variation of the TiO_2 loading in NC namely 0, 30, 50 and 70 % (w/w). These photocatalysts were called NCT, NCT 70-30, NCT 50-50, NCT 30-70 respectively. Before photodegradation, the samples were placed in a photoreactor without being exposed to a UV lamp for 1 hour to ensure adsorption-desorption equilibrium on the NCT surface. The recyclability of the NCT photocatalyst is carried out by separating the NCT solid from the solution, then drying it and finally reusing it for further experiments.

3. Results and Discussion

Figure 1 presents the SEM characterization and EDX results of NCT. It can be stated that the composite has been formed due to the presence of C, O and Ti elements in the NCT. Figure 2 presents the photodegradation of paracetamol as a function of time using the CNT photocatalysts and bare CT under UV light as photon source. None of NCT composites showed noticeable adsorption phenomena during 1 hour before starting the degradation process, showing that the elimination of paracetamol was barely affected by the adsorption. From figure 2, it can be seen that the more TiO_2, the greater the decrease in paracetamol concentration. This result demonstrated that TiO_2 plays a key role in waste degradation [11], [15] and NC's function is more about a supporting material. This photocatalyst can be easily separated from the waste and reused when the NCT composite in the solid form. When 70% w/w TiO_2 is loaded in NC (NCT 30-70), there is no agglomeration and electron-hole separation proceeds smoothly, allowing recombination to be avoided. Better photocatalyst efficacy and efficiency are the outcome of this phenomena.

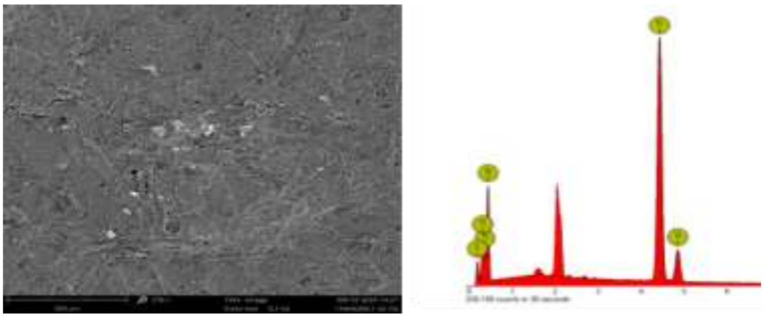

Figure 1 SEM characterization and EDX results of NCT 30-70

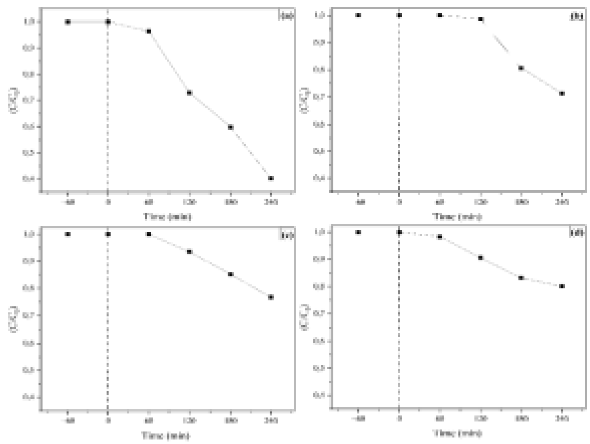

Fig 2. Photocatalytic degradation of paracetamol by a) NCT 30-70, b) NCT 70-30, c) NCT 50-50 and d) NCC at pH = 6 where Co is the initial concentration and C is concentration of paracetamol at time (t)

The effectiveness of the photodegradation of several contaminants, including paracetamol, is known to be significantly influenced by pH [16]. For this reason, the impact of pH on photodegradation was assessed at various pH values, and Figure 3 displays the findings. The optimal photocatalytic activity for the NCT 30-70 nanocomposites was achieved at pH = 6 under UV irradiation.

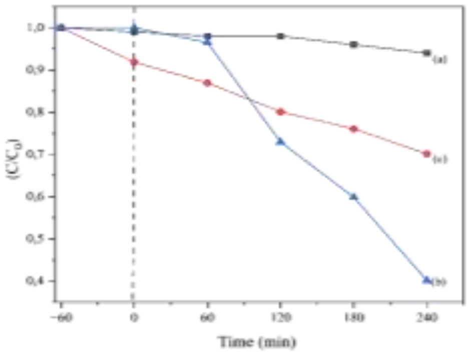

Fig 3. The photodegradation efficiency of paracetamol with different pH for NCT 30-70 at different pH value (a) pH 3, (b) pH 6, (c) pH 9

There was an increase in the effectiveness of paracetamol photodegradation from acidic condition (pH=3) to nearly neutral (pH=6). This can be influenced by speciation of TiO_2 metal. Under acidic conditions TiO_2 forms more $Ti(OH_2)^+$. This species is difficult to release OH radicals, so that the effectiveness of photodegradation is low. At nearly neutral pH, TiO_2 in the form of TiOH species which relatively easily releases OH radicals, resulting in effectiveness photodegradation is higher when compared to acidic conditions. Under alkaline conditions, TiO_2 in the form of TiO^-, which is relatively more difficult to form OH radicals. Therefore, it can be seen in figure that at pH 3 and 9 there was a decrease in the effectiveness of paracetamol photodegradation compared to pH 6 [17].

Figure 4 shows the recyclability of the NCT photocatalyst for NCT 30-70. After photodegradation, the sample was recovered from the solution by filtration using Whatman filter paper No.1 and finally dried at 40^oC for 24 hours. Then, the composite was reused for a new paracetamol photodegradation experiment. Figure 4 illustrates that the C/Co was 40% during the initial use and went up until the third use when it reached C/Co = 0.62. The primary cause of this could be the unavoidable loss of trace amounts of photo-active material (TiO_2) during separation from solution following each run. But the C/Co dropped from 0.62 to 0.53 on the fourth use. The fourth use's lower paracetamol concentration might have resulted from the NCF composite shrinking in size as a result of stirring, which caused a significant amount of TiO_2 to be liberated from the nanocellulose. In these circumstances, NCT's surface area increases, improving its photodegradation efficiency.

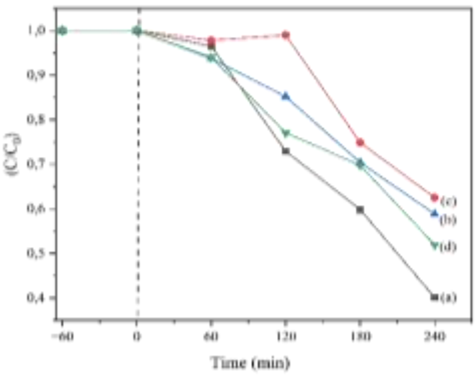

Fig 4. Evaluation of the paracetamol degradation over UV irradiation NCT 30-70 for four times consecutive usage A) first time usage, B), second time usage C) third time usage and D) forth time usage

4. Conclusions

A straightforward technique, the sonication-assisted impregnation approach, has been effectively used to create a nanocellulose/TiO_2 (NCT) solid composite, as proven by SEM characterization.

Nanocellulose was extracted from EPOB by the hydrolysis method at low sulfuric acid concentration. TiO_2 loading in NC and pH influence the effectiveness of paracetamol photodegradation. The prepared NCT nanocomposite showed promising application in pollutant photodegradation, and the optimum results for this study were obtained with the NCT 30-70 photocatalyst at pH 6. Under these conditions, the C/Co value was around 40%. The NCT solid composite can be reused up to four times in applications, but its effectiveness is reduced, which may be due to some of the TiO_2 being released from the solid composite.

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