Development of Chitosan/TiO2 Nanocomposite for Multifunctional Sunscreen Application

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Abstract. Several problems that often occur on the skin are acne and sunburn due to UV exposure. Acne is caused by the activity of bacteria dwelling on the surface of skin. This study has successfully synthesized several multifunctional cream based on chitosan loading in the chitosan/TiO2 nanocomposite. Multifunctional sunscreen defined by anti-bacterial and sunscreens performance with photocatalytic technology. Multifunctional sunscreen is made by Chitosan/TiO2 nanocomposite as active ingredient. Nanocomposite which has been synthesized is characterized by FT-IR, UV-Vis DRS, and SEM-EDX. To make Multifunctional sunscreen, the nanocomposite chitosan/TiO2 as active ingredient is mixed with water and carboxymethyl cellulose (CMC) as natural emulsifier. The result of testing the disinfection of bacteria Escheria coli by nanocomposite chitosan/TiO2 showed the bacteria can be eliminated up to 99.7% within 2 hours. As sunscreens, creams have the ability to moderate protection under UV rays with SPF values from 21.30 to 22.77.

1. Introduction
Indonesia as one of the tropical country in southeast asia, has a quite high sun exposure around 1800-2000 kWh/m³ per year. Continous exposure of UV light contained in sunrays can do serious damage to the skin, or people might call it sunburn. On critical condition is that extensive exposure of ultraviolet radiation can cause skin cancer.

Sunscreen generally has two types based on the protection properties offered, namely physical sunscreen and chemical sunscreen. Physical sunscreen functions is to drive UVA and UVB rays out of the skin by reflecting it on the surface of the skin. Physical sunscreen protection mechanism can work immediately after being applied on the skin and to obtain maximum protection, the application of physical sunscreen must be evenly distributed to all parts of the body but often leaves white spots after use. This encourages the creation of new sunscreen performance that leaves no white files but is able to work as a sunscreen. Chemical sunscreen can answer this problem, chemical sunscreens work by filtering and absorbing UV light and turning it into heat energy released through the skin. This causes a chemical sunscreen to be applied 20 minutes before being in the sun, because the content takes time to absorb into the skin. In the chemical sunscreen the utilization of the content of titanium oxide / titania (TiO2) and zinc oxide (ZnO2) as UV filters is very often found in the community. On the other hand, titania and zinc oxide can release ROS (Reactive Oxygen Species) in the form of radical hydroxyl compound, into the skin so that it can potentially cause irritation, itching, and redness.
Chitosan is a compound synthesized by de-acetylation of shrimp skin and able to reduce ROS compounds to Glucosamine and Chito-oligosaccharides which do not cause irritation, itching and redness in the skin (Chang, 2001). Chitosan also has anti-bacterial properties (Goy R.C, 2009). Chitosan itself comes from the skin of crustacean living things and is often found in the fishing industry. The export value of the fisheries industry in the shrimp sector increased by 34% from 2008 (Fronthea Swastawati, 2008) made an increase in shrimp waste because the byproducts in the form of head, skin, and tail of shrimp were around 30% -50% of initial weight. It can be concluded that shrimp skin has a lot of availability and its use in Indonesia as a processed material from waste is still minimal. Therefore, the key objective of this study is by making a composite of titania and chitosan to multifunctional sunscreens that do not cause irritation, itching, and redness when applied to the skin while being anti-bacterial.

2. Experimental

2.1. Materials
Aquades, Chitosan Analytical Grade (De-acetylation degree >75%), Acetic Acid (CH3COOH), Nitric Acid (HNO3), TiO2 Evonik P25, and Methylene Blue.

2.2. Methods
Titania / Chitosan composite synthesis using Wet Impregnation Method. The first step is by making a 5% acetic acid solution of 10 mL, then adding HNO3 solution until it reaches pH 3. Chitosan compounds are added to the mixture as much as loading variations (0%; 0.5%; 1%; 5%; and 10%). Next adding Titania to the chitosan solution and stirred manually, after that sonication for 30 minute required. The solution then separated using centrifuge and washed with distilled water until pH 7 was obtained from Titania / Chitosan solution. Furthermore, the composite was dried using a magnetic stirrer for 2 hours at 800C. The dried composites were then crushed using mortar to obtain a fine catalyst powder.

3. Result and Discussion

3.1. Characteristic of Nanocomposite
The FTIR spectrum of several Chitosan/TiO2 nanocomposite (% Chitosan based on weight) is shown in Figure 1. To see whether a bond between chitosan and TiO2 has occurred, functional group peak that shows the presence of chitosan is needed, according to Shahida (2016) the presence of chitosan can be seen in the 1500 nm wave number peak which indicates the presence of NH- bonds in the chitosan chain, then at wave number 3400 nm which indicates the presence of an -OH bond. The presence of a peak at wave number 1177 nm shows the stretching and bending of the CH3 group, Ti-O-C bond, or Ti-OH (Kavitha, et al. 2013).

![Figure 1. FTIR Spectrums of the Nanocomposite](image-url)
For 1% chitosan loading, 3% chitosan, 5% chitosan, and 10% chitosan have similar and identical wave number ranges found in the four samples, namely in the wavelength region 1637 - 1440 nm and 3211 - 3227 nm. For wave number 3211 - 3227 nm shows the vibration of the hydroxyl group (\(-\text{OH}\)) which shows the occurrence of bonding from the chitosan hydrogen group to TiO\(_2\) (Fajriati, 2014). The spectrum of wave numbers 1637 - 1440 nm also shows the presence of H\(^+\) atomic bonds from amino groups (NH2) from chitosan structures that make hydrogen bonds to titania groups (Fajriati, 2014). Therefore, it can be concluded that the possible bond between chitosan and titania is a hydrogen bond.

The results in table 1. show that the response of Chitosan/TiO\(_2\) nanocomposite is better to receive photon energy compared to Chitosan 0%/TiO2. The reduction in gap energy by chitosan showed that chitosan/TiO2 nanocomposite would be more easily activated by photon energy than normal TiO2. After acquiring the band gap energy from table 1, Kubelka-Munk analysis can be used to determine the light wavelength needed by the nanocomposite to be activated. The result can be seen in table 1, the energy gap values of chitosan/TiO2 nanocomposite are decreasing as the addition of chitosan loading which initially, chitosan0%/TiO2 has a gap energy value 3.17 to 3.08 on chitosan10%/TiO2 nanocomposite. Even though the reduction in gap energy is not too significant, still when applying in daily activities to chitosan/TiO2 sunscreen, it can help activate TiO2 under sun exposure. This can occur because chitosan / TiO2 nanocomposite can be responsive with wavelengths up to 402.53 cm\(^{-1}\). Chitosan here is acting as if it was dopant for TiO2, when metal dopant usually attracting the electrons which produced when photocatalysis occurred, chitosan is reacting with hole (h\(^+\)) produced by photocatalysis so that the recombination for electrons and hole can be minimized, so the band gap of TiO2 are reduced[7].

| Sample       | Band Gap Energy (eV) | Wavelength (nm) |
|--------------|-----------------------|-----------------|
| Chitosan0%/TiO2 | 3.17                  | 391.10          |
| Chitosan1%/TiO2 | 3.13                  | 396.10          |
| Chitosan3%/TiO2 | 3.11                  | 398.70          |
| Chitosan5%/TiO2 | 3.09                  | 401.53          |
| Chitosan10%/TiO2 | 3.08                  | 402.53          |

Characterization of SEM (Scanning Electron Microscopy) was carried out to determine the morphology and structure. The nanocomposite characterized by SEM / EDX was loading Chitosan3%/TiO2. The results of which can be seen in Fig. 3. In Fig. 3 (a) it can be seen that one of the matrix formations of chitosan / TiO2 nanocomposite. White powder covering the aggregate surface is TiO2 nanoparticles, the aggregate is estimated to be chitosan. This is reinforced by the next image (b) with a 5 times magnification at the same point, where the EDX results show the part that is not covered in white powder (B), the C atom is detected more than the Ti atom while the part covered by white powder (A) shows an increase in Ti atoms compared to C atoms. As seen in Table. 2 for comparison.

**Table 1. Band Gap Energy and Activation Wavelength**

**Figure 2.** Morphology of Chitosan 3%/TiO2 at 25.000x
Table 2. EDX Result on Sample Chitosan 3%

| Elements      | (A)(%Wt) | (B)(%Wt) |
|---------------|----------|----------|
| Carbon (C)    | 6.06     | 13.74    |
| Oxygen (O)    | 29.38    | 35.16    |
| Titanium (Ti) | 64.58    | 51.10    |

3.2. Performance of Nanocomposite

3.2.1. Decolorization of Methylene Blue. Decolorization of MB testing was carried out to see the ability of Chitosan/TiO2 nanocomposites to reduce the activity of ∙OH radical compounds to degrade colors as a representation of human skin which can be irritated by radical compounds ∙OH. This test uses five samples, namely chitosan loading 0%, loading 1%, loading 3% loading 5%, and loading 10%. Methylene blue is used as a colored organic compound, the test is carried out using a photoreactor for one hour per sample by taking data in 0, 15, 30, and 60 minutes. Percentage of color degradation is then seen through the value of methylene absorbance resulting from degradation compared to the absorbance early methylene blue.

On Figure 5(a) and Figure 5(b) it can be seen that the degradation of methylene blue is best done by nanocomposites with 0% chitosan loading or 93.5% TiO2 within 1 hour, the mechanism that occurs in this event is photocatalysis, where when the energy of a photon excites TiO2 produces an electron pair and hole. Holes that are positively charged oxidize hydroxyl compounds or water compounds, then produce OH (∙OH) radicals. This hydroxyl compound can later degrade methylene blue into other compounds. But according to Zuo (2014) methylene blue is not directly degraded to CO2 and H2O but through a series of reactions, where when methylene blue encounters electrons from TiO2 it will become methylene blue radicals which can be degraded by ∙OH radicals thus losing methylene blue constituent elements such as C, N, S, to become CO2 and H2O. The loading variation of 1% to 10% has decreased due to the presence of chitosan compounds which are able to reduce OH radical formation through the mechanism of binding of hydrogen peroxide compounds to glucosamine compounds and chitooligosaccarides (Chang, et al., 2001). Decreasing the percentage of degradation of methylene blue along with increasing chitosan loading proves that the more chitosan compounds, OH radical activity can be reduced. The mechanism of suppressing OH radical activity as follows:

\[
(GlcN)_m - (GlcN)_n + OH \bullet \rightarrow (GlcN \bullet)_m - (GlcN)_n + H_2O \quad (1)
\]

\[
(GlcN \bullet)_m - (GlcN)_n + H_2O \rightarrow (GlcN) + (GlcN) \quad (2)
\]

Table 3. MB Decolorization percentage at 1 hours of each nanocomposite

| Chitosan/TiO2 | %A/A0 when 60 Minutes |
|--------------|-----------------------|
| 0% (TiO2)    | 93.5%                 |
| 1%           | 92.6%                 |
| 3%           | 91.1%                 |
| 5%           | 84.6%                 |
| 10%          | 77.0%                 |

3.2.2. Antibacterial Activity. In Figure 6 it can be seen that samples with chitosan loading have the ability to disinfect bacteria more effectively than samples that are not given chitosan (0%). This proves that the addition of chitosan is able to improve the disinfection ability of TiO2 bacteria. This disinfection process can occur due to two things, the first by the photocatalytic activity of TiO2 itself and the antibacterial properties possessed by chitosan. The disinfection process through photocatalytic activity occurs because TiO2 is activated by photon energy in this case in the form of UV light and then
photocatalytic activity results in • OH radicals or can also be referred to as ROS (Reactive Oxygen Species) compounds, then ROS compounds react with bacterial cell membranes so that causing bacterial cells to leak causing the molecular molecules inside the cell to come out, making the cell unable to move again and then die. This degradation process continues until the cell nucleus makes the bacteria break down completely into CO2 and H2O. (Sangchay et al., 2013) (Tsai et al., 2012).

Figure 3. Morphology of Chitosan 3%/TiO2 at 25.000x

Chitosan also helps the bacterial disinfection process, besides helping to facilitate the activation of TiO2 by UV light, chitosan also has antibacterial properties that are able to simultaneously disinfect bacteria along with photocatalytic activity. According to Goy, R.C (2009) the mechanism of the antibacterial chitosan involves the interaction between chitosan molecules that are positively charged with a negatively charged bacterial membrane. The interaction makes two results. The internal osmotic imbalance of bacterial cells is due to changes in the permeability properties of bacterial cell membranes thereby inhibiting bacterial cell growth. Leakage of electrolyte fluid contained in bacterial cells due to peptidoglycan hydrolysis in bacterial cell membranes. This model has been evaluated by Raafat et, al (2008). using an electron microscope to see the ultrastructural changes of bacterial cells when they are exposed to positively charged chitosan. He found the presence of chitosan molecules still attached to the membrane of dead bacterial cells. Therefore, with minimal light or no light, chitosan / TiO2 nanocomposites can still disinfect bacteria by the presence of chitosan. It can be seen also from the results of 100% chitosan loading without TiO2 proving that chitosan indeed has antibacterial properties.

3.2.3. Sun Protection Factor Performance. Sun Protection Factor or SPF testing is used as a parameter to determine how well synthesized sunscreens can work in absorbing UV light. The higher the SPF value, the more effective it is to protect the skin from the adverse effects of UV light (Dutra et al., 2004). The SPF value can be interpreted as the amount of UV energy needed to achieve. MED (Minimal Erythematic Dose) on skin given sunscreen compared to the amount of UV energy needed to reach MED on sun-protected skin (FDA, 2001). In this test, the method used is the Mansur method, where using the value of absorbance of sunscreen between wavelength ranges of 290 nm - 320 nm (UV-B) at intervals of 5 nm then processed into SPF values using the existing equations. To use the Mansur method, the value of Correction Factor (CF) is obtained from commercial sunscreens that have known SPF values. In this study, the correction factor value used refers to research from Taqqiyah, Shofi (2012) that has been predetermined to facilitate calculations.
Table 4. SPF Value on Each Nanocomposite

| Chitosan/TiO<sub>2</sub> | SPF Value |
|-------------------------|-----------|
| 0%                      | 21.30     |
| 1%                      | 21.66     |
| 3%                      | 21.77     |
| 5%                      | 21.42     |
| 10%                     | 21.46     |

Based on the calculation of the SPF value above, it can be concluded that the addition of chitosan loading does not make the SPF value differ significantly. The SPF value generated is consistently in the range 21.3-21.4. In this case chitosan / TiO<sub>2</sub> nanocomposite is in accordance with previous results where the addition of chitosan can reduce the bandgap energy of TiO<sub>2</sub> when viewed from Figure 7. Chitosan0% / TiO<sub>2</sub> has the lowest SPF value compared to other loading variations, this proves the addition of chitosan is able to increase TiO<sub>2</sub> response in absorbing UV / photon light. Chitosan3% / TiO<sub>2</sub> has the highest SPF value compared to other variations, this can occur Chitosan3% / TiO<sub>2</sub> is the most effective composition in the performance of chitosan / TiO<sub>2</sub> nanocomposite because the least shading effect on chitosan / TiO<sub>2</sub> nanocomposite occurs, so that UV light / energy of photons entering the surface of TiO<sub>2</sub> is not blocked by chitosan and is proven by the best performance of bacterial disinfection in these nanocomposites.

4. Summary
From the experimental data we can conclude that: Wet Impregnation Method is proven to be one of the methodology of synthesizing Chitosan/TiO<sub>2</sub> nanocomposite. In FT-IR result emphasize that under the certain range of wave number the most significant bonds between TiO<sub>2</sub> and Chitosan are Amino group attached from Chitosan and O from TiO<sub>2</sub>[5]. Under UV-Vis spectroscopy test, implied that Chitosan also reduce the band gap energy from TiO<sub>2</sub> making TiO<sub>2</sub> more active when irradiated with certain type of light[7]. Antibacterial activity also generated by Chitosan/TiO<sub>2</sub> nanocomposite until the loading of 3% chitosan in the composite. SPF value which generated are classified in high protection of sunlight class by Indonesian Government (SNI 164-399-1996). Based on those two performance test the most optimal chitosan loading on TiO<sub>2</sub> is loading with a concentration of 3% chitosan / TiO<sub>2</sub>.

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