Sodium alginate-TiO₂-bentonite nanocomposite synthesis for photocatalysis of methylene blue dye removal

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Abstract. In this study, nanocomposite based on biopolymer using sodium alginate (NaAlg) and bentonite intercalated by TiO₂ was synthesized. Bentonite in the nanocomposite was used as a template for TiO₂ nanoparticles formation through in-situ method and NaAlg was used as catalyst supporter in order to obtain nanocomposite material, which was expected as dye waste removal. The nanocomposite was characterized using Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray (EDX) and Tunneling Electron Microscopy (TEM). The obtained nanocomposite had TiO₂ average nanoparticles size around 35 nm. Nanocomposite was applied for photocatalysis to remove the dye waste of methylene blue (MB). Degradation percentage was achieved at 90.50 % with the optimum condition at pH 8 with photocatalysis time at 30 min and 30 mg nanocomposite mass. Biopolymer-based sodium alginate and TiO₂-bentonite nanocomposite can be applied to reduce dyestuff that is biodegradable and environmentally friendly waste.

Keywords: biopolymers, bentonite, catalyst, nanocomposite, sodium alginate

1. Introduction
Society’s high demand of textile causes the textile industry to grow massively and carries negative impacts for human beings and environment. Recently, one of the utmost concerns is how to handle the environmental pollution, especially in water, due to the wastewater from textile industry. Wastewater that contains dye is very dangerous because most dyes are hard to be degraded, resistant, and toxic [1]. One of the most used dyes is methylene blue (MB), which is a non-biodegradable organic pollutant caused by the presence of benzene groups that are difficult to be degraded, in which its exposure will cause asphyxiation, vomiting, diarrhea, and nausea [2]. Therefore, to prevent the risk, some efforts to remove dye in environment should be taken.

Some techniques can be done to treat dye waste, such as adsorption and photocatalysis. These techniques are widely used because adsorption is easier to be applied, low-cost and have a high uptake. However, the adsorption process only absorbs waste toxic and it will not be degraded into non-toxic compounds. Meanwhile, photocatalysis technique is widely used because it can decompose toxic into non-toxic compounds. This is due to in photocatalytic process a lot of hydroxyl radical that attacks dye organic into CO₂, H₂O, and other non-toxic substances will be formed, so it will be environmentally friendly [3].

In the photocatalyst process, the used materials have the ability to absorb photons and usually owned by semiconductor materials. Metal semiconductor materials such as TiO₂, ZnO, Fe₂O₃, CdS, and ZnS can be utilized as catalysts in a photocatalytic process. The most widely used semiconductor for photocatalysis is titanium dioxide (TiO₂), due to its stability under UV-light. In this study, bentonite as filler is used due to the high adsorption capacity of its porous structure [4–6].
Utilization of the biopolymer as nanocomposite has caught attention of many researchers around the globe; the cause is its biodegradable properties and decreases the needs for synthetic polymer. One of the biopolymers that have many advantages is alginate, which extracted from brown algae. Alginate is a renewable and biodegradable natural polymer, which has high capacity to remove toxic pollutants such as dye waste [7–9]. Some researches have made some attempts to treat waste using composite such as Harikumar et al. [7], who has succeeded to degrade some dyes using calcium alginate-TiO₂ composite through adsorption and photocatalytic process. Laysandra et al. [10] has successfully reduced methylene blue and rhodamine B dye wastes through photocatalytic and adsorption process.

In this study, nanocomposite was done by combining sodium alginate, bentonite with inorganic substances to obtain nanocomposites that have superior property, derived from sodium alginate and bentonite having large surface area, high pores and good degradation properties of TiO₂, so that obtained a maximum photocatalytic power in reducing methylene blue dyestuff. In this work, the effect of nanocomposite mass (10, 20, 30, and 40 mg), photocatalysis time (1 h with 10 min interval), and the effect of pH (3, 7, 8, and 9) of methylene blue solution have been studied.

2. Experimental

2.1. Materials
Materials used were titanium tetraisopropoxide, TTIP (Merck Co) as the precursor of TiO₂; ethanol p.a. (Merck Co) as solvents; HCl (Merck Co) as a catalyst in TiO₂ synthesis; sodium alginate (Sigma) and bentonite (Sigma Aldrich) as nanocomposite components; HNO₃ (Merck Co) as a catalyst for TiO₂-bentonite composite synthesis; CaCl₂ (Merck Co) to form beads on nanocomposite; HSO₃ (Merck Co) as bentonite activator and dye acidity controller, NaOH (Merck Co) to control dye basicity; methylene blue (Merck Co) as the dye to be tested.

2.2. TiO₂ synthesis
TiO₂ has been synthesized according to previous reports [11]. The precursor of titanium tetraisopropoxide (TTIP) was added into distilled water, ethanol, HCl and then stirred at room temperature and dried. The solid was calcinated at 450 °C for 2 h. The nano TiO₂ was characterized by Fourier Transform Infrared (FTIR) and Scanning Electron Microscopy (SEM).

2.3. Sodium alginate-TiO₂ synthesis
The synthesis of sodium alginate-TiO₂ was performed using ex-situ method [12]. TiO₂ (2 wt.%) and sodium alginate (2 wt.%) was stirred, then added with 0.5 M CaCl₂ solution to form beads of NaAlg-TiO₂. The beads were dried in an oven at 30 °C for 1 h. The sodium alginate-TiO₂ was characterized by FTIR and SEM.

2.4. Bentonite-TiO₂ synthesis
The synthesis of TiO₂-bentonite was performed using in-situ method [12,13]. TTIP was dropped into ethanol and stirred for 30 minutes, and then it was added into HNO₃ until TiO₂ sol was formed. Furthermore, bentonite was added to the solution and stirred, the solid was dried and calcinated at 500 °C. The TiO₂-bentonite was characterized by FTIR and SEM.

2.5. Synthesis of sodium alginate-TiO₂-bentonite nanocomposite
The synthesis of sodium alginate-TiO₂-bentonite referred to previous reports [5]. The sodium alginate was dissolved in distilled water and added with TiO₂-bentonite, then stirred until the solution homogenous, and it was injected into CaCl₂ solution. The obtained solid was dried at 50 °C for 1 h and the nanocomposite of sodium alginate-TiO₂-bentonite was characterized by FTIR, Scanning Electron Mircoscopy-Energy Dispersive X-Ray (SEM-EDX) and Tunneling Electron Microscopy (TEM).

2.6. Photocatalysis Activity
The activity of photocatalysis was tested against methylene blue solution, performed by the three types of nanocomposite (sodium alginate-TiO₂; bentonite-TiO₂; sodium alginate-TiO₂-bentonite) by referring to previous reports [5]. Photocatalysis process was conducted for 1 h with UV light, and analyzed for every 10 min using UV-Vis spectrophotometer. The degradation capacity or removal capacity of methylene blue catalytic process by nanocomposite was calculated using the following equation:

\[
\text{The degradation capacity} \, (\%) = \left( \frac{C_i - C_f}{C_i} \right) \times 100
\]
most of O content derived from sodium alginates, monomers and bentonite. While, Si and Al are from nanocomposite. There are O, C, Si, Ti, Al, etc. (41.7, 19.3, 11.2, 9.2, 5.1 and 13.5 wt.%), it shows at TiO\textsubscript{2}.

Figure 2b shows the morphology of TiO\textsubscript{2}.

Figure 2d shows the morphology of TiO\textsubscript{2}, sodium alginate-TiO\textsubscript{2}-bentonite nanocomposite

where C\textsubscript{i} is initial concentration of methylene blue (ppm) and C\textsubscript{e} is methylene blue concentration at equilibrium (ppm).

3. Results and discussion

3.1. FTIR Analysis

Figure 1a shows the absorption of infrared of TiO\textsubscript{2}, sodium alginate-TiO\textsubscript{2}, (figure 1b) bentonite-TiO\textsubscript{2}, (figure 1c) and sodium alginate-TiO\textsubscript{2}-bentonite nanocomposite (figure 1d). In figure 1a, we can see the absorption peak of TiO\textsubscript{2} at 590 cm\textsuperscript{-1} indicating the stretching and bending vibrations of Ti-O-Ti [14]. Figure 1b shows that absorption peak around 3150-3600 cm\textsuperscript{-1} which is O-H stretching vibration of hydroxyl groups, weak absorption band at 2937 cm\textsuperscript{-1} shows C-H stretching. The peaks at 1400 and 1628 cm\textsuperscript{-1} shows symmetric and asymmetric O-C-O stretching vibrations and at 500-700 cm\textsuperscript{-1} is characteristic for Ti-O-Ti from TiO\textsubscript{2} (b). Figure 1c shows the absorption band at 3150-3600 cm\textsuperscript{-1} indicating the O-H stretching vibration of Ti-OH and Si-OH interacted with water molecules to form hydrogen bond. It also appears a peak of Si-O-Ti at 965 cm\textsuperscript{-1}. In figure 1d, we can see the absorption band at 3250-3600 cm\textsuperscript{-1} indicating O-H stretching vibration, and the weak absorption band at 2937 cm\textsuperscript{-1} which is characteristic for the C-H stretching. The peaks at 1475 and 1645 cm\textsuperscript{-1} indicating the asymmetric and symmetric stretching of carboxylate O-C=O [15]. There is also a peak at 1035 cm\textsuperscript{-1} refers to C-O stretching of uronic acid and the peak at 820 cm\textsuperscript{-1} is the absorption band of C-H vibration mannuronic acid and peaks at 550 cm\textsuperscript{-1} indicating the presence of Ti-O-Ti bond and we can see peak of TiO\textsubscript{2} at 500 cm\textsuperscript{-1}, whereas at pure TiO\textsubscript{2} showed at 590 cm\textsuperscript{-1}, shift of peak shows that the TiO\textsubscript{2} have been successfully impregnated in nanocomposite.

3.2. SEM and EDX analysis

Surface characterization using SEM is shown in figure 2. Figure 2a shows the morphology of sodium alginate, we can see short fibers are distributed evenly, which is the characteristic of sodium alginate. Figure 2b shows the morphology of TiO\textsubscript{2}, and have small granules shape. Figure 2c is the morphology of bentonite, there are pores so that causes a good adsorption ability. Meanwhile, figure 2d shows the morphology of NaAlg-TiO\textsubscript{2}-Bentonite, it can be observed the presence of fibrous derived from sodium alginate and the pores from bentonite. There are TiO\textsubscript{2}, as small granules particles on the surface of sodium alginate and in the pores bentonite. This shows the successful synthesis of the nanocomposite.

Figure 3 shows EDX analysis of NaAlg-TiO\textsubscript{2}-Bentonite. It can be observed the content of elements in nanocomposite. There are O, C, Si, Ti, Al, etc. (41.7, 19.3, 11.2, 9.2, 5.1 and 13.5 wt.%), it shows at most of O content derived from sodium alginates, monomers and bentonite. While, Si and Al are from
Figure 2. Surface morphology of (a) sodium alginate; (b) TiO$_2$; (c) bentonite and (d) sodium alginate-TiO$_2$-bentonite nanocomposite.

Figure 3. EDX analysis of sodium alginate-TiO$_2$-bentonite nanocomposite.

Figure 4. Micrograph of NaAlg-TiO$_2$-Bentonite nanocomposite at resolution of 100 nm.
bentonite. The content of Ti is 9.2 wt.% in peak appears in three peaks at 0.2, 4.3 and 4.9 keV. The EDX data supports the successful synthesis of NaAlg-TiO$_2$-bentonite nanocomposite.

3.3. TEM analysis

Characterization using transmission electron microscopy (TEM) with 100 nm resolutions can be seen in sodium alginate-TiO$_2$-bentonite nanocomposite in figure 4. We can see the surface morphology of the TiO$_2$ nanoparticles are small, black particles with TiO$_2$ in average size around 35 nm and bentonite as templates shows gray color and sodium alginate as a supporting agent with brighter color can be observed. This supports the results of the previous characterization showing the success of nanocomposite synthesis.

3.4. Photocatalysis activity

The photocatalysis activity was done by determining the best composite. There are three types of nanocomposites have been synthesized (NaAlg-TiO$_2$, bentonite-TiO$_2$ and NaAlg-TiO$_2$-Bentonite). Each of nanocomposite was performed the degradation process against methylene blue (MB). Degradation capacity of MB in three types of nanocomposites is shown in figure 5a. The methylene blue before the degradation process have dark blue color and after the photocatalysis process, it got paler. We could see that the percentage of degradation sequence of methylene blue for the three types of nanocomposites is NaAg-TiO$_2$ (69.05 %) < Bentonite-TiO$_2$ (79.10 %) < NaAlg-TiO$_2$-Bentonite (90.50 %), respectively. The greater the percent of degradation, the solution will be clearer. This is caused by the nanocomposite of NaAlg-TiO$_2$-Bentonite have strong adsorption ability derived from sodium alginate and bentonite and combination of TiO$_2$ have good degradation ability and obtained the best degradation capacity. For the next optimization, the best nanocomposite of NaAlg-TiO$_2$-Bentonite was used. Figure 5b shows the effect of NaAlg-TiO$_2$-Bentonite nanocomposite mass to MB degradation capacity in the photocatalysis process. We can see the percentage of degradation capacity MB increased with rise of the nanocomposite mass and reached an optimum at 30 mg in 90.50 %. Furthermore, the increase of mass more than 30 mg, caused no significant change to degradation capacity.

Figure 5c shows the time effect to the degradation capacity of MB on photocatalysis process. We can see the percentage of degradation capacity MB increased with the rise of time and reached an

![Figure 5](image-url)
optimum time at 30 min, which obtained 90.10%, and then with the increase of time, there is no significant change to degradation capacity. Figure 5d shows the degradation capacity of MB increased with the rise of pH. In acidic condition, the excessive H+ ion in solution causes the active site of nanocomposites surface creates electrostatic repulsion between H+ ions and methylene blue cationic with the nanocomposites surface. Therefore, the amount of adsorbed methylene blue will decrease. The reaction estimation of the active site of TiO2 in acidic condition can be seen in equation (2). In base condition or the pH of the solution increases, the photocatalytic process will increase with the rise of pH. This is due to the change of charge of TiO2, in a high pH, TiO2 would be negatively charged. Furthermore, the increase of OH group would increase OH radicals. Therefore, since methylene blue is a cationic dye, there will be attraction between the negatively charged nanocomposite surfaces with positively charged of methylene blue, so that at high pH, photodegradation effectiveness would be increased [16]. The optimum degradation capacity was obtained with condition of pH 8. The reaction estimation of the active site of TiO2 in base condition is shown in equation (3).

\[
\begin{align*}
\text{pH (acid)} & : Ti - OH + H^+ \rightarrow TiOH^+_2 \\
\text{pH (basic)} & : Ti - OH + OH^- \rightarrow TiO^- + H_2O
\end{align*}
\]

The best degradation capacity using sodium-alginate-TiO2-bentonite nanocomposite for the degradation of methylene blue obtained at nanocomposite mass 30 mg, photocatalysis time 30 min and pH 8 was 90.10%. The results of this degradation showed better results than our previous work with 51.68% degradation [16].

4. Conclusions

Among some composites that have been synthesized, NaAlg/TiO2/bentonite composite has the best ability to degrade methylene blue. The success of nanocomposite synthesis was supported by characterization of FTIR, SEM, EDX and TEM. EDX characterization shows that TiO2 has the composition of 9.2 wt.% with particle size 35 nm according to TEM characterization. The percentage of degradation sequence of methylene blue for the three types of nanocomposites is NaAg-TiO2 (69.05%) < Bentonite-TiO2 (79.10%) < NaAlg-TiO2-Bentonite (90.50%), respectively. NaAlg-TiO2-bentonite nanocomposite has the best ability to degrade methylene blue. The optimal photocatalysis conditions obtained at 30 mg nanocomposite mass for 30 min at pH 8 is 90.50% of methylene blue have been degraded.

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