Adsorption and Photodegradation of Cationic and Anionic Dyes by TiO₂-Chitosan Nanocomposite

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Abstract: The adsorption and photodegradation of cationic and anionic dyes by TiO₂-chitosan nanocomposites have been studied. This study investigated the specific surface area, pores volume, pores size of TiO₂-Chitosan nanocomposite, and determination kinetics of the reaction on the adsorption and photodegradation process. The methods were carried out by mixing TiO₂-nanocomposite into cationic and anionic dyes in various contact times and initial dye concentrations. The results showed that nanocomposite adsorption capacity increased with an increase in the amount of chitosan (TiO₂/Chit 0.13) even though the specific surface area (SBET) was reduced. The results indicated that the adsorption on nanocomposite was influenced by the amount of -NH₂ and -OH on the chitosan surface. The maximum adsorption capacity (qₘ) and the observed reaction constant (kₐₜₘ) for MO were also known to be higher than MB, which means that the TiO₂-chitosan nanocomposites could remove anionic dye more than cationic one.

Keywords: adsorption; photodegradation; cationic dye; anionic dye

INTRODUCTION

The increasing use of dyes in many industries had become an important problem because dyes had a serious and harmful ecosystem effect on aquatic life. Dyes have been extensively used in the textile, paper, printing, carpet, plastic, food and cosmetic industries. Therefore, intensive efforts to eliminate the dye from wastewater have gained a major concern [1].

There is a wide range of treatment technologies to remove dyes from wastewater, including physical methods (filtration, sedimentation, and distillation), chemical methods (coagulation, adsorption, photodegradation, ozonation, and ion exchanges), and biological methods using microorganism to remove dyes via aerobic-anaerobic degradation. However, such processes still have significant disadvantages, such as the requirement of waste disposal sites and additional advanced treatments to reduce waste toxicity. Furthermore, the treatment of liquid waste using such methods may take a longer time, as well as high energy requirements and high cost. The microorganism was also ineffective to delocalize the wastewater since most of the dyes were synthesized in nature, which makes them difficult to be naturally degraded by microorganism [2].

TiO₂ photocatalyst method has been developed for wastewater treatment, because of some advantages, of which TiO₂ photocatalyst can degrade harmful organic waste, detoxify heavy metals, and at the same time, deactivate microorganism. TiO₂ photocatalyst is also a non-toxic and cheap wastewater treatment, and quite stable in many conditions such as in various pH and temperature.

TiO₂ photocatalyst performance could be improved, one of which was immobilized in supporting material. Chitosan was an excellent adsorbent, as well as was used as supporting material. Anatase TiO₂ had been successfully synthesized in situ in chitosan to form TiO₂-chitosan nanocomposite. The Nanocomposite was
reported to have a synergy effect in removing dyes through adsorption and photodegradation process [3]. Chitosan as the supporting material had also increased the photocatalytic activity in removing dyes because the chitosan was good adsorbent. The combination of photodegradation and adsorption process had increased the effectiveness of removing dyes in wastewater [4]. Therefore, TiO$_2$-chitosan nanocomposite could be used to remove dye wastewater through the adsorption and photodegradation process.

This research aims to study the adsorption and photodegradation process of dyes in TiO$_2$-chitosan nanocomposite. The adsorption and the photocatalytic process of the composites were separately evaluated and reaction conditions including contact time and various concentration of dyes were systematically investigated. The differences in the adsorption properties of the composites were intensively investigated based on the analysis using Langmuir adsorption isotherm. The dyes used in this study were methylene blue as a cationic dye (basic dye) and methyl orange as an anionic dye (acidic dye). Those dyes were widely used in textile industries and potentially hazardous to the water environment.

Methylene blue (MB) is one of the positively charged basic dye (usually amine salts or ionized imines) because MB ionized Cl$^-$ [5], and the other hand, methyl orange (MO) is an acidic dye with negative charge (usually organic sulfonate group, RSO$_2$O$^-$) because MO ionized Na$^+$ in solution [6]. The molecular structure of methylene blue (MB) and methyl orange (MO) was shown in Fig. 1.

![Fig 1. The molecular structure of (a) methylene blue and (b) methyl orange](image)

**Instrumentation**

The chitosan solution was prepared by dissolving 3 g chitosan in 100 mL acetic acid 1%, followed by vigorous stirring at room temperature for 24 h using magnetic stirrer at 600 rpm (Cimarec Barnstead Thermolyne). Centrifugation was carried out using Boeco C-28 Centrifuge (Model BOE 1205-13, Boeckel & Co, Hamburg, Germany) and oven (Thermoline Electric from Heraeus) was used for the drying process. The photocatalytic decolorization of MO and MB was conducted using a closed photoreactor equipped with magnetic stirrer and a UV lamp (40 W) operated at 290–390 nm.

**Procedure**

*The preparation of TiO$_2$ Sol by aging at room temperature*

The chitosan solution was prepared by dissolving 3 g chitosan in 100 mL of 1% acetic acid solution, followed by vigorous stirring at room temperature for 24 h. Fifty milliliters of titanium(IV) isopropoxide (TTIP) was added dropwise into 500 mL of deionized water containing 50 mL of acetic acid solution, under vigorous stirring at room temperature for 24 h. The obtained mixture was labeled as TTIP sol. Freshly prepared TTIP sol was then stored without stirring at room temperature and atmospheric pressure. It became transparent within one week.

*Preparation of TiO$_2$–chitosan nanocomposites and TiO$_2$ powders*

The TTIP sol was used to prepare TiO$_2$-chitosan nanocomposites by sol-gel technique. Different amount of TTIP sol was added to the 3% (w/v) of chitosan solution to reach the desired concentrations of TTIP (mol/L): 0.13, 0.33, 0.65 and 1.3, under vigorous stirring...
Table 1. The composition of chitosan and TTIP in the TiO\textsubscript{2}-chitosan nanocomposites

<table>
<thead>
<tr>
<th>Chitosan (g)</th>
<th>TTIP (mL)</th>
<th>Nanocomposite Types</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>1.0</td>
<td>TiO\textsubscript{2}/Chit 0.13</td>
</tr>
<tr>
<td>3.0</td>
<td>2.5</td>
<td>TiO\textsubscript{2}/Chit 0.33</td>
</tr>
<tr>
<td>3.0</td>
<td>5.0</td>
<td>TiO\textsubscript{2}/Chit 0.65</td>
</tr>
<tr>
<td>3.0</td>
<td>10.0</td>
<td>TiO\textsubscript{2}/Chit 1.3</td>
</tr>
</tbody>
</table>

at room temperature for 24 h. The resulted nanocomposites were then stored without stirring at room temperature and atmospheric pressure for two weeks (14 days). The nanocomposites were then dried at 80 °C for 60 min in a preheated oven. Finally, the nanocomposites were washed with distilled water until pH 6–7 and then dried again at 80 °C for 60 min in a preheated oven. The TTIP concentration of 0.13, 0.33, 0.65 and 1.3 mol/L were used to prepare different TiO\textsubscript{2}-chitosan nanocomposites. The samples were afterward labeled as TiO\textsubscript{2}/Chit 0.13, TiO\textsubscript{2}/Chit 0.33, TiO\textsubscript{2}/Chit 0.65 and TiO\textsubscript{2}/Chit 1.3 respectively.

The composition and type of nanocomposites were given in Table 1.

The adsorption process

The Brunauer-Emmett-Teller (BET) surface areas of the nanocomposites were determined by nitrogen adsorption-desorption isotherms measured on a Quantachrome NovaWin 2 analyzer. All samples had been previously degassed before the actual measurements. The adsorption process was examined by mixing 20 mL of dye solution containing MO (20 mg/L) and MB (10 mg/L), with 0.02 g of each TiO\textsubscript{2}-chitosan nanocomposite type, within various contact time. The experiment was carried out in a reactor with dark conditions (without light) to examine the adsorption of dyes on the nanocomposite surface, and in a reactor with light conditions (with UV light) to determine the photodegradation of dyes. The effect of contact time, with and without the light, is shown in Fig. 2–5.

The percentage of degraded dyes significantly increased for the first three hours, before it slowed down and became constant (Fig. 2 and 3). The slow degradation and tendency of being constant could be attributed to the depletion of dyes in solution. In the dark conditions, the removal of dyes in solution was mostly caused by adsorption on the surface of the nanocomposite. The Nanocomposites containing small amounts of TiO\textsubscript{2} had produced higher adsorption because the free site active groups such as NH\textsubscript{2} and -OH were much more on chitosan. The dye adsorption on chitosan formed coordination bonds resulted from interfacial interactions between the base sites (NH\textsubscript{2})

The photodegradation process

The photodegradation process was conducted by mixing 0.02 g of each TiO\textsubscript{2}-chitosan nanocomposite (TiO\textsubscript{2}/Chit 0.13, TiO\textsubscript{2}/Chit 0.33, TiO\textsubscript{2}/Chit 0.65 and TiO\textsubscript{2}/Chit 1.3) with 20 mL of MO (10, 20, 30, 40 and 50 mg/L) and MB (5, 10, 15, 20 and 25 mg/L) in an Erlenmeyer flask. The mixture was placed in the photoreactor equipped with a UV lamp (40 W) at 290–390 nm, and it was allowed to react at different contact time (1–8 h, with 1 h interval). The MO and MB solution was then by UV spectrometry at 464 nm.

RESULTS AND DISCUSSION

The study of adsorption and photodegradation properties were conducted separately by preparing four types of nanocomposites with different ratio of TiO\textsubscript{2} and chitosan (labeled as TiO\textsubscript{2}/Chit 0.13, TiO\textsubscript{2}/Chit 0.33, TiO\textsubscript{2}/Chit 0.65 and TiO\textsubscript{2}/Chit 1.3). Those nanocomposites were studied in several adsorption conditions, including various contact times and initial concentrations of dye.

The Effect of Contact Time

The effect of contact time to the dye adsorption and photodegradation was analyzed by reacting 20 mg/L MO and 10 mg/L MB with 0.02 g of each TiO\textsubscript{2}-chitosan nanocomposite type, within various contact time. The experiment was carried out in a reactor with dark conditions (without light) to examine the adsorption of dyes on the nanocomposite surface, and in a reactor with light conditions (with UV light) to determine the photodegradation of dyes. The effect of contact time, with and without the light, is shown in Fig. 2–5.

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available on chitosan and Lewis acid sites from titanium [7]. Therefore, increasing the amount of TiO₂ in nanocomposites had resulted in fewer sites of –NH₂ and -OH in chitosan. Thus, the nanocomposite TiO₂/Chit 0.13 had the highest adsorption activity and the lowest photodegradation process. The dye adsorption on –NH₂ and -OH groups in chitosan was higher than in TiO₂.

**The Effect of the Initial Concentrations of Dye Solution**

The initial concentration of dye solution had influenced the adsorption and photodegradation as it involved the amount of reacted pollutant (Fig. 3 and 4). The increasing concentrations enhanced the amount of adsorbed and degraded dyes until the increase rate became insignificant or constant. High adsorption on the photocatalyst surface could enhance the photodegradation process. However, if the increase in dye concentration was too high, the nanocomposite would be saturated because the adsorption capacity was exceeded [8]. In addition, if the dye concentration is too high, the photodegradation could be reduced because abundant dyes could block the penetration of light into TiO₂. Therefore, the adsorption and photodegradation process was not significantly influenced by the dyes which had a too high concentration.
The Adsorption of Cationic and Anionic Dyes by TiO$_2$-Chitosan Nanocomposite

The adsorption of cationic and anionic dyes on nanocomposite occurred when the dyes interacted directly in a particular time. The dye adsorption on nanocomposite surface was investigated under dark conditions (without light).

**BET analysis**

BET analysis was conducted to determine the specific surface area, which this property corresponds to the adsorption capacity of the nanocomposite. The BET analysis resulted from the four nanocomposites types with chitosan and TiO$_2$ bulk as references, as shown in Fig. 6.

According to the Brunei-Deming-Teller (BDDT) classification, the chitosan bulk graph was found to be of a sigmoid type and BET classification of type 2, which was solid-nonporous materials. On the other hand, the TiO$_2$ bulk followed the type 4, with the specific flow of hysteresis loop for mesoporous material that resulted in a large surface area [9].

Nevertheless, the nonporous material such as chitosan had a rather strong adsorbent-adsorbate interaction due to the presence of -NH$_2$ and -OH active groups. Table 2 showed the characters of porous chitosan
bulk, TiO₂ bulk and types of TiO₂-chitosan nanocomposite, including the specific surface area, the total pore volume and the average pore diameter, using the Brunauer-Emmet-Teller (BET) method.

The specific surface area, the total pore volume, and the pore size were increased by a higher amount of TiO₂ in the nanocomposite. Conversely, the reduced number of TiO₂ could decrease the specific surface area, because the pore particles of TiO₂ were covered by bulk chitosan [10].

According to the classification by BDDT, the adsorption-desorption isotherm graphs of TiO₂/Chit 1.3
Table 2. The BET analysis of TiO$_2$-chitosan nanocomposites

<table>
<thead>
<tr>
<th>Nanocomposite type</th>
<th>Specific surface area ($S_{BET}$) (m$^2$/g)</th>
<th>Total pore volume (cm$^3$/g($\times10^{-2}$))</th>
<th>Pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan Bulk</td>
<td>0.63</td>
<td>9.8x10$^{-4}$</td>
<td>15.257</td>
</tr>
<tr>
<td>TiO$_2$ Bulk</td>
<td>138.31</td>
<td>39.10</td>
<td>47.02</td>
</tr>
<tr>
<td>TiO$_2$/Chit 1.3</td>
<td>29.76</td>
<td>4.08</td>
<td>20.22</td>
</tr>
<tr>
<td>TiO$_2$/Chit 0.65</td>
<td>25.50</td>
<td>3.79</td>
<td>18.92</td>
</tr>
<tr>
<td>TiO$_2$/Chit 0.33</td>
<td>1.42</td>
<td>1.34</td>
<td>15.25</td>
</tr>
<tr>
<td>TiO$_2$/Chit 0.13</td>
<td>0.54</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

and TiO$_2$/Chit, 0.65 nanocomposites tended to follow type 4 with the specific flow of the hysteresis loop for mesoporous material. Meanwhile, the TiO$_2$/Chit 0.33 and TiO$_2$/Chit 0.13 nanocomposites appeared to follow the type 1 and type 2, which was specific to the solid-nonporous material and microporous.

The N$_2$ adsorption-desorption graph of TiO$_2$/Chit 0.65 and TiO$_2$/Chit 1.3 nanocomposites showed, that under the low condition of relative pressure ($P/P_0$), the desorption and desorption graphs did not overlap. This unusual case could occur in metastable materials such as chitosan. These properties were indicated by the presence of interconnected pores like a tinted bottle and the random pore distribution. Therefore, the desorption process could happen through percolation mechanism, of which that enclosed the outflow of the gas phase from the pores. The confined gasses in the pores was accumulated and would be released out simultaneously under low pressure. As a result, the adsorption-desorption graph showed that more gases were desorbed than adsorbed.

**Adsorption isotherm**

Some adsorption isotherm models were studied to understand the adsorption process. One of the adsorption isotherm models is the Langmuir isotherm model. The equation for Langmuir adsorption isotherm is as follows [12-13]:

$$C_e = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$$

$C_e$ is the concentration of dyes (MO and MB) in solution (mg/L), $K_L$ is the Langmuir constant that associated to the adsorption energy (L/mg), $q_e$ is the amount of dye absorbed per 1 g of catalyst (mg/g), and $q_m$ is the maximum adsorption capacity (mg/g). The adsorption isotherm graph was used to define the adsorption equilibrium time or the adsorption capacity, which was determined through various contact time, as shown in Fig. 4 and Fig. 5.

Based on the adsorption isotherm graph in Fig. 7, the maximum adsorption capacity ($q_m$) value and the adsorption equilibrium constant ($K_L$) of the nanocomposite to dye molecules could be calculated from the equation of line curve $C_e/q_m$ versus $C_e$ (Table 2). The Fig. 7 showed that the adsorption of dyes by nanocomposite followed the Langmuir isotherm model, suggested that each pollutant of MO and MB was specifically bound to the nanocomposite surface in monolayer and homogenous dispersion.

Table 3 pointed out that the nanocomposites had a stronger interaction with MO than MB, as indicated by the higher maximum adsorption capacity ($q_m$) and Langmuir equilibrium constant ($K_L$) against MO than against MB. This occurred because MO was an anionic dye that could interact electrostatically with the protonated -NH$_2$ on the nanocomposite, while MB was a cationic dye that could produce repulsing force due to the same electric charge. The adsorption of negatively charged MO occurred through the electrostatic attraction to protonated -NH$_2$ [12], while the adsorption toward the positively charged MB occurred due to the attraction of hydrogen bond and ion exchange with -OH groups [13].

Increased maximum adsorption capacity ($q_m$) was not always linear with increasing specific surface area (SBET) (Fig. 8). Nanocomposite containing the highest amount of TiO$_2$ had the largest SBET, while the
Table 3. The adsorption isotherm constants of TiO$_2$-chitosan nanocomposite for MO and MB

<table>
<thead>
<tr>
<th>Nanocomposite Types</th>
<th>q$_m$ (x 10$^2$ (mg/g))</th>
<th>K$_L$ (L/mg)</th>
<th>R$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$/Chit 0.13</td>
<td>6.66</td>
<td>6.69</td>
<td>0.34</td>
</tr>
<tr>
<td>TiO$_2$/Chit 0.33</td>
<td>5.71</td>
<td>4.25</td>
<td>0.22</td>
</tr>
<tr>
<td>TiO$_2$/Chit 0.65</td>
<td>4.34</td>
<td>3.33</td>
<td>0.13</td>
</tr>
<tr>
<td>TiO$_2$/Chit 1.33</td>
<td>2.70</td>
<td>1.92</td>
<td>0.11</td>
</tr>
</tbody>
</table>

The Photodegradation of Cationic and Anionic Dyes Catalyzed by TiO$_2$-Chitosan Nanocomposite

The photodegradation process was initiated with the adsorption of dyes on the surface of nanocomposites. Under the UV radiation at 340–390 nm (3.0–3.65 eV), the adsorbed dyes reacted to radical OH$^•$ with h$^+$ as an oxidizing agent, or a charge transfer that produces photocatalytic products was occurred [14]. The UV radiation at 340–390 nm gives out sufficient energy needed by TiO$_2$ photocatalyst to gather photoactive species, which are e$^-$ ($\approx$ electron) and h$^+$ ($\approx$ hole or positively charged species due to the electron lost) on the surface of TiO$_2$ photocatalyst. This phase is called the oxidizing generation phase.

Fig 7. The adsorption isotherm of TiO$_2$-chitosan nanocomposite for MO (a) and MB (b)

Fig 8. The relationship between specific surface area (S$_{BET}$) with maximum adsorption capacity (q$_m$) for MO and MB (Graph of A is TiO$_2$/Chit 1.3; B is TiO$_2$/Chit 0.65; C is TiO$_2$/Chit 0.33, and D is TiO$_2$/Chit 0.13)

The mechanism of photodegradation of MO and MB by TiO$_2$-nanocomposite chitosan under UV radiation as illustrated in Fig. 9 (adapted from Nawi...
The mechanism consists of 3 phases that occur simultaneously. The first phase, the adsorption of anionic dye (MO) on the nanocomposite surface was through electrostatic attraction between sulfoxide (-SO3-) of MO molecule and protonated amine (-NH3+) of chitosan, while the adsorption of cationic dye (MB) occurred through electrostatic attraction between electrons of MB molecules in aromatic ring and -NH3+ group of chitosan. Adsorption of MB was weaker because of the repulsing force between positive charges from MB and -NH3+ in chitosan [16].

In the second phase, TiO2 which had absorbed UV light could produce holes (h+) in the valence band (h+(VB)) and e- in the conduction band (e-(CB)). The reaction on the surface of the TiO2 photocatalyst is:

\[
2 (\text{VB}) (\text{CB}) \text{TiO}_2 \rightarrow \text{TiO}_2^* + h^+ + e^- \]

The h+(VB) was reacted with aqueous and produced a strong OH radical:

\[
h^+_{(VB)} + \text{OH}^- \rightarrow \text{OH}^\cdot
\]

\[
h^+_{(VB)} + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+
\]

Dye molecules adsorbed on the surface of TiO2 nanocomposite could be oxidized:

\[
\text{MO/MB} + h^+_{(VB)} \rightarrow \text{oxidation product}^*
\]

\[
\text{MO/MB} + \cdot\text{OH} \rightarrow \text{oxidation product}^*
\]

\[\left( \cdot\text{CO}_2, \text{H}_2\text{O} \text{ and mineral} \right)\]

In the third phase, h+ on the surface of TiO2 diffuses into the chitosan surface and attacks MO/MB molecules on chitosan surface. The MO/MB molecule is positively charged, which could initiate photodegradation reactions, as follows:

\[
\text{MO}^{\text{ad}}/\text{MB}^{\text{ad}} + h^+ \rightarrow \text{MO}^{\text{ad}}^* / \text{MB}^{\text{ad}}^* + \text{H}^+
\]

\[
\text{MO}^{\text{ad}}^* / \text{MB}^{\text{ad}}^* + \text{TiO}_2 \rightarrow \text{MO}^{\text{ad}} + / \text{MB}^{\text{ad}} + + \text{TiO}_2 (e^-_{(CB)})
\]

Meanwhile, e-(CB) had reacted with dissolved oxygen (O2) to produce OH, O2-, HO2 or H2O2 radicals. Recombination between h+(VB) and e-(CB) was also prevented by this reaction, therefore photodegradation of dyes was increased [17-18].

**The effect of TiO2 weight in photodegradation process**

Addition of the amount of TiO2 in TiO2-chitosan nanocomposite could increase the number of h+, OH and e- radical, therefore the degradation of MO and MB also increased. However, the excess weight of TiO2 could
reduce photodegradation of dyes (Fig. 10).

MO and MB photodegradation occurred until the weight of TiO$_2$ reached a certain amount, around 45% (TiO$_2$/Chit 0.65). The excess weight of TiO$_2$ had caused some TiO$_2$ to be outside the chitosan matrix; therefore chitosan could limit the growth of TiO$_2$ particles. TiO$_2$ particles outside the chitosan matrix had a large particle size because they were aggregated. This had caused the light absorbed by TiO$_2$ to be partly because the one exposed to light was the surface of TiO$_2$ only [19].

**The kinetics of MO and MB photodegradation**

The kinetic photodegradation of dyes by TiO$_2$ nanoparticles was still a crucial issue. Some researchers reported that the kinetics of the photodegradation reaction followed the Langmuir-Hinshelwood model (L-H model). The validity of the L-H model in interpreting photodegradation reactions was easier to understand [20-21].

The kinetics of MO and MB Photodegradation was a function of the ratio of the concentration of dyes and time. Measurements were conducted in a solution of 20 mg/L MO and 10 mg/L MB. The effect of the ratio of initial concentration (Co) and concentration after t (min) (Ce) during photodegradation was shown in Fig. 11.

Fig. 11 showed that the photodegradation rate of MO and MB followed the first order (pseudo) reaction. This was because the reaction rate depended on the reactants concentration at low dye concentrations. The kinetic constant (k) is determined by the Langmuir-Hinshelwood (L-H) equation, as follows [22]:

\[
\frac{dr}{dt} = -\frac{kK_L C_0}{1 + K_L C_e} = \ln \left( \frac{C_0}{C_e} \right) + K_L (C_0 - C_e) = kK_L t
\]

r is the reaction rate, C$_0$ is the initial concentration, C$_e$ is the concentration after t, with t represent the reaction time (min), K$_L$ is the Langmuir adsorption constant, and

**Fig 10.** The effect of TiO$_2$ weight in nanocomposite to dye removal (Graph of A is TiO$_2$/Chit 0.13; B is TiO$_2$/Chit 0.33; C is TiO$_2$/Chit 0.65; and D is TiO$_2$/Chit 1.3)

**Fig 11.** (a) Langmuir-Hinshelwood kinetic of MO photodegradation (b) Langmuir-Hinshelwood kinetic of MB photodegradation
k is the kinetic constant (min\(^{-1}\)). If \(K_c C_e << 1\), then \(r = k K_c C_e\) with the limits of integration are \(C_e = C_0\) at \(t = 0\) and \(C_e = C_e\) at \(t = t\). Then, the equation of L–H can be simplified into the first order reaction, as follows:

\[-\ln \frac{C_e}{C_0} = k_{\text{obs}} t\]

\(k_{\text{obs}}\) was the observed kinetic constant (min\(^{-1}\)) and \(k_{\text{obs}} = k K_c\). The kinetic parameter of \(k_{\text{obs}}\) was determined by fitting the curve of \(-\ln C_e/C_0\) vs \(t\), and the observed kinetic constant was determined based on the slope value of the graph regression equation. The graph describing the observed kinetic constant (\(k_{\text{obs}}\)) in the photodegradation of MO and MB were given in Fig. 12.

Fig. 12 showed that photodegradation of MO and MB followed a (pseudo) first-order reaction. The (pseudo) first-order reaction is a rate reaction depends linearly on the concentration of the dyes. When adsorption was one of the kinetic determinant parameters, the kinetic constant (\(k\)) that had been affected by the adsorption process was determined by the \(k_{\text{obs}} = k K_c\) equation. The parameters of the observed kinetic constant rate (\(k_{\text{obs}}\)) did not consider the adsorption during heterogeneous photocatalytic reactions. The \(k\) value was given in Table 4.

Table 4 showed that the highest observed kinetic (\(k_{\text{obs}}\)) was achieved by TiO\(_2\)/Chit 0.65, while the highest corrected kinetic (\(k\)) was achieved by TiO\(_2\)/Chit 1.3. The TiO\(_2\)/Chit 0.65 nanocomposite had the highest observed kinetic (\(k_{\text{obs}}\)) because it has the highest \(E_g\) value and the highest crystallinity [19]. On the other hand, the TiO\(_2\)/Chit 1.3 nanocomposite had the highest corrected kinetic (\(k\)) because the adsorption equilibrium constant (\(K_L\)) value of TiO\(_2\)/Chit 1.3 was the lowest, hence the time needed by dyes to achieve the adsorption equilibrium on the TiO\(_2\)/Chit 1.3 nanocomposite was shorter. The relationship between TiO\(_2\) weight in nanocomposite and observed kinetic (\(k_{\text{obs}}\)) in MO and MB photodegradation is given in Fig. 13.

Fig. 13 indicated that the increasing weight of TiO\(_2\) in the nanocomposite enhances the photodegradation rate. The excess TiO\(_2\) content in nanocomposite produced more OH radicals. It was beneficial to improve

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**Fig 12.** (a) Observed kinetic constant (\(k_{\text{obs}}\)) of MO photodegradation follows the first order reaction (b) Observed kinetic constant (\(k_{\text{obs}}\)) of MB photodegradation follows the first order reaction

**Table 4.** The photodegradation rate parameters of MO and MB catalyzed by TiO\(_2\)-chitosan nanocomposite

| Nanocomposite Types | \(k_{\text{obs}}\) (min\(^{-1}\)) | \(K_c\) (L/Mg) | \(k\) (x 10\(^2\) (min\(^{-1}\))) |
|---------------------|----------------|--------------|----------------|----------------|
| TiO\(_2\)/Chit 0.13 | 100.5 | 97.13 | 0.034 | 0.028 | 2.951 | 3.396 |
| TiO\(_2\)/Chit 0.33 | 104.6 | 103.5 | 0.022 | 0.016 | 4.670 | 6.347 |
| TiO\(_2\)/Chit 0.65 | 146.9 | 158.4 | 0.013 | 0.011 | 10.57 | 13.89 |
| TiO\(_2\)/Chit 1.3 | 130.5 | 144.2 | 0.011 | 0.008 | 11.64 | 16.58 |
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Fig 13. The relationship between TiO₂ weight with the kinetics (k) of MO and MB photodegradation nanocomposites performance as a photocatalyst, because much more OH radicals had been able to increase photodegradation reactions.

The different kinetics in various levels of TiO₂ (Fig. 11) indicated different activation energy between nanocomposites. The energy activation affected the rate reaction. When the catalytic reaction occurred in constant temperature, thus the kinetic was only influenced by the activation energy (Eₐ) [22].

Two determining factors for the activation energy in nanocomposite were the weight of TiO₂ and the distribution of TiO₂ in the nanocomposite. Based on different energy activations in the nanocomposite, it was predicted that the distribution of TiO₂ in nanocomposite followed two types. First, TiO₂ was distributed closed in the chitosan matrix space. Second, TiO₂ was distributed inside and outside the chitosan matrix.

The first type occurred in the nanocomposites containing low TiO₂ weights, (as TiO₂/Chit 0.13 and TiO₂/Chit 0.33), while the second type occurred in the nanocomposite containing high TiO₂, (as in TiO₂/Chit 0.65 and TiO₂/Chit 1.3). The distribution of TiO₂ inside and outside the chitosan matrix had a higher photodegradation than when TiO₂ was in the chitosan matrix. This result was confirmed by the increase in photodegradation reaction kinetic.

CONCLUSION

TiO₂–chitosan nanocomposite was a photocatalyst that could remove cation (MB) and anion (MO) dyes by adsorption and photodegradation processes. Photodegradation of MO was greater than MB. MO was also more easily absorbed by nanocomposite than MB because MO had electrostatic attraction as a driving force. The adsorption process was dominant when the weight of TiO₂ in nanocomposite was low due to higher amounts of -OH and -NH₂ in the chitosan matrix. The photodegradation kinetics of MO and MB followed a first-order reaction. The highest kinetic constant (k) is obtained by the largest TiO₂ nanocomposite.

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