Adsorption and Photodegradation of Cationic and Anionic Dyes by TiO_2-Chitosan Nanocomposite

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Abstract: *The adsorption and photodegradation of cationic and anionic dyes by TiO_2-chitosan nanocomposites have been studied. This study investigated the specific surface area, pores volume, pores size of TiO_2-Chitosan nanocomposite, and determination kinetics of the reaction on the adsorption and photodegradation process. The methods were carried out by mixing TiO_2-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 (TiO_2/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 -NH_2 and -OH on the chitosan surface. The maximum adsorption capacity (q_m) and the observed reaction constant (k_{Obs}) for MO were also known to be higher than MB, which means that the TiO_2-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].

TiO_2 photocatalyst method has been developed for wastewater treatment, because of some advantages, of which TiO_2 photocatalyst can degrade harmful organic waste, detoxify heavy metals, and at the same time, deactivate microorganism. TiO_2 photocatalyst is also a non-toxic and cheap wastewater treatment, and quite stable in many conditions such as in various pH and temperature.

TiO_2 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 TiO_2 had been successfully synthesized in situ in chitosan to form TiO_2-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_2O^-) because MO ionized Na^+ in solution [6]. The molecular structure of methylene blue (MB) and methyl orange (MO) was shown in Fig. 1.

EXPERIMENTAL SECTION

Materials

Titanium(IV) isopropoxide (TTIP) was obtained from Sigma–Aldrich. Acetic acid 99.8% and methyl orange ($C_{14}H_{14}O_3N_3SNa$) was obtained from Merck. Chitosan (with 87% degrees of deacetylation) was obtained from Biotech Surindo, Cirebon, Indonesia. Distilled water and deionized water were obtained from Pharmaceutical Laboratories Jakarta. All chemicals were of reagent grade.

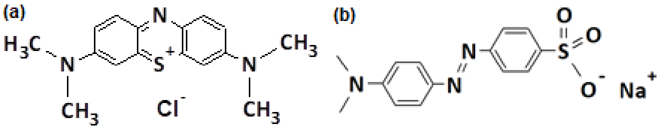

Fig 1. The molecular structure of (a) methylene blue and (b) methyl orange

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_2-chitosan nanocomposites

Chitosan (g)	TTIP (mL)	Nanocomposite Types
3.0	1.0	TiO_2/Chit 0.13
3.0	2.5	TiO_2/Chit 0.33
3.0	5.0	TiO_2/Chit 0.65
3.0	10.0	TiO_2/Chit 1.3

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_2-chitosan nanocomposites. The samples were afterward labeled as TiO_2/Chit 0.13, TiO_2/Chit 0.33, TiO_2/Chit 0.65 and TiO_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_2-chitosan nanocomposite (TiO_2/Chit 0.13, TiO_2/Chit 0.33, TiO_2/Chit 0.65 and TiO_2/Chit 1.3) in an Erlenmeyer flask. The mixture was placed in a reactor with dark conditions. The mixture was allowed to react at different exposure time (1–8 h, with 1 h interval). Afterward, the mixture was centrifuged at 3000 rpm for 5 min. The filtrate was then measured by UV-Vis at 464 nm to identify the removal of dye before and after mixing with nanocomposite. The same procedure was applied to different concentrations of MO (10, 30, 40 and 50 mg/L) and MB (5, 15, 20 and 25 mg/L).

The photodegradation process

The photodegradation process was conducted by mixing 0.02 g of each TiO_2-chitosan nanocomposite (TiO_2/Chit 0.13, TiO_2/Chit 0.33, TiO_2/Chit 0.65 and TiO_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_2 and chitosan (labeled as TiO_2/Chit 0.13, TiO_2/Chit 0.33, TiO_2/Chit 0.65 and TiO_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_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_2 had produced higher adsorption because the free site active groups such as NH_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_2)

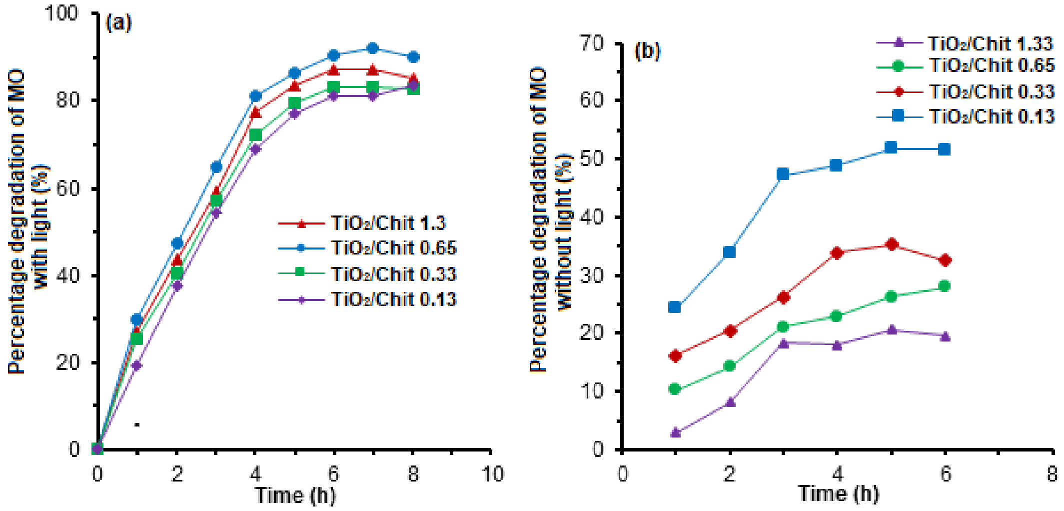

Fig 2. The effect of contact time on the adsorption and photodegradation of MO with light (a) and without light (b)

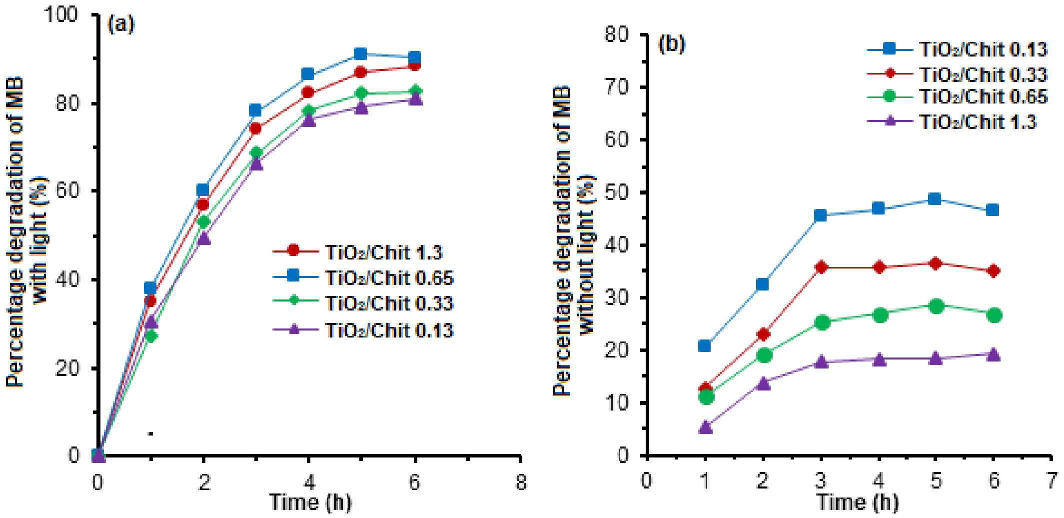

Fig 3. The effect of contact time on the adsorption and photodegradation of MB with light (a) and without light (b)

available on chitosan and Lewis acid sites from titanium [7]. Therefore, increasing the amount of TiO_2 in nanocomposites had resulted in fewer sites of $-NH_2$ and -OH in chitosan. Thus, the nanocomposite TiO_2/Chit 0.13 had the highest adsorption activity and the lowest photodegradation process. The dye adsorption on $-NH_2$ and -OH groups in chitosan was higher than in TiO_2.

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 TiO_2. Therefore, the adsorption and photodegradation process was not significantly influenced by the dyes which had a too high concentration.

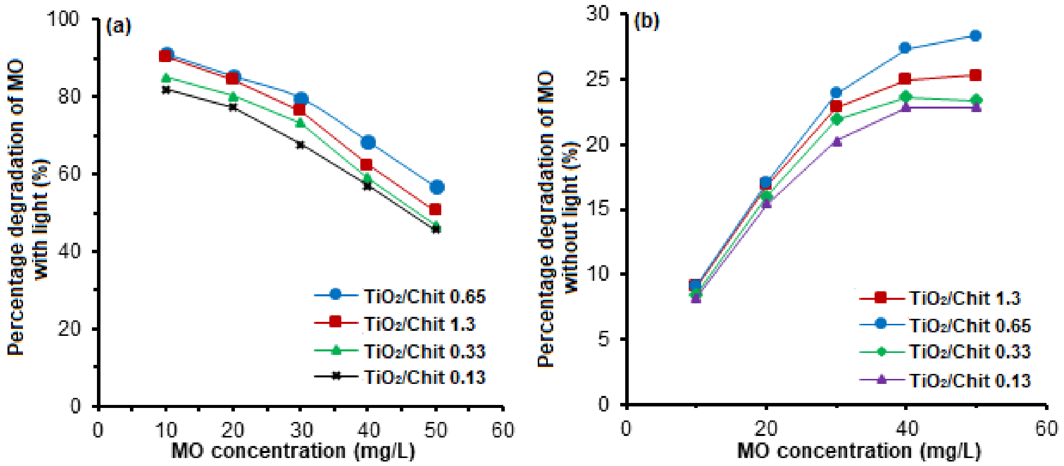

Fig 4. The effect of initial dye concentration on the adsorption and photodegradation of MO with light (a) and without light (b)

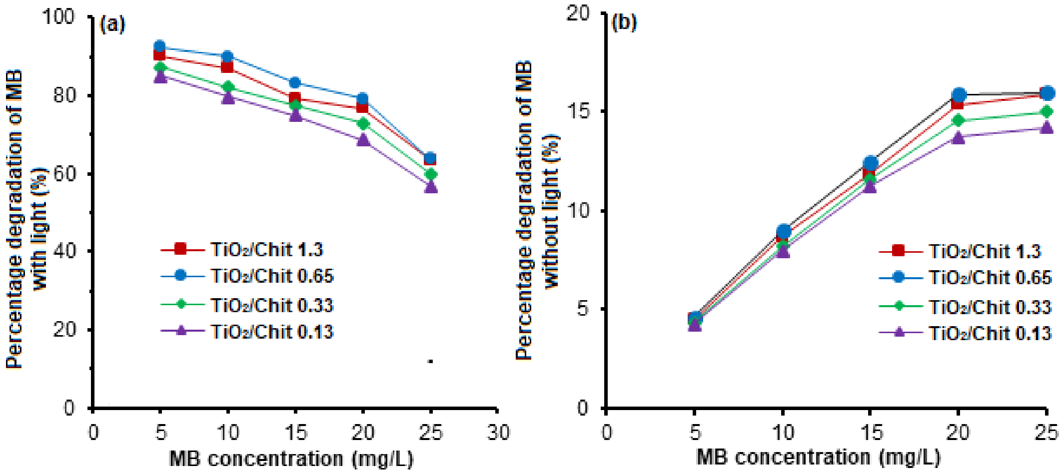

Fig 5. The effect of initial dye concentration on the adsorption and photodegradation of MB with light (a) and without light (b)

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

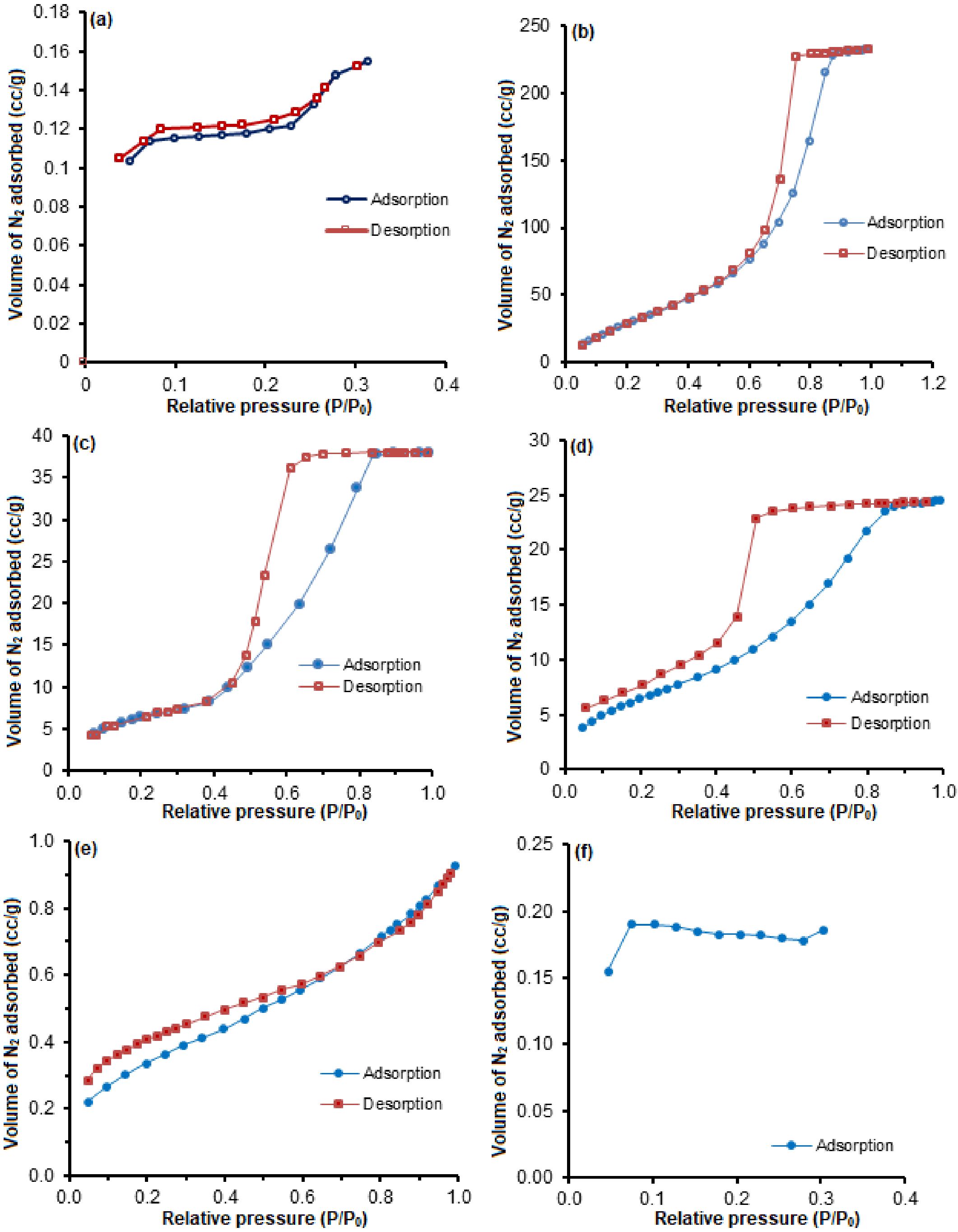

Fig 6. The N_2 adsorption – desorption isothermic graph of Chitosan (a); TiO_2 bulk (b); TiO_2/Chit 1.3 (c); TiO_2/Chit 0.65 (d); TiO_2/Chit 0.33 (e); TiO_2/Chit 0.13 mol/L (f)

bulk, TiO_2 bulk and types of TiO_2-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 pores size were increased by a higher amount of TiO_2 in the nanocomposite. Conversely, the reduced number of TiO_2 could decrease the specific surface area, because the pore particles of TiO_2 were covered by bulk chitosan [10].

According to the classification by BDDT, the adsorption-desorption isotherm graphs of TiO_2/Chit 1.3

Table 2. The BET analysis of TiO_2-chitosan nanocomposites

Nanocomposite type	Specific surface area (S_{BET}) (m^2/g)	Total pore volume (cm^3/g)(x 10^{-2})	Pore diameter (Å)
Chitosan Bulk	0.63	$9.8x10^{-4}$	15.257
TiO_2 Bulk	138.31	39.10	47.02
TiO_2/Chit 1.3	29.76	4.08	20.22
TiO_2/Chit 0.65	25.50	3.79	18.92
TiO_2/Chit 0.33	1.42	1.34	15.25
TiO_2/Chit 0.13	0.54	-	-

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 [11].

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]:

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

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

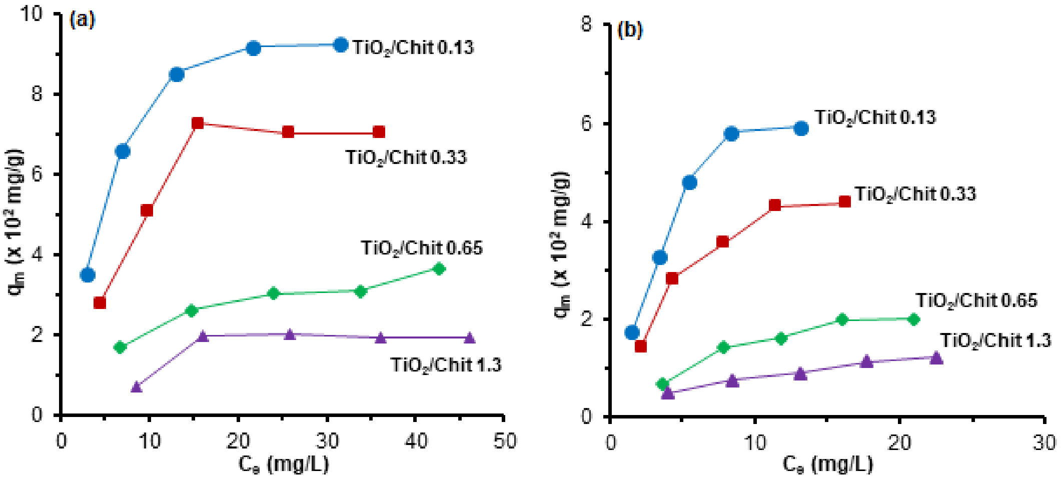

Fig 7. The adsorption isotherm of TiO_2-chitosan nanocomposite for MO (a) and MB (b)

Table 3. The adsorption isotherm constants of TiO_2-chitosan nanocomposite for MO and MB

Nanocomposite Types	q_m (x 10^2 (mg/g))		K_L (L/mg)		R^2	
	MO	MB	MO	MB	MO	MB
TiO_2/Chit 0.13	6.66	6.69	0.34	0.22	0.929	0.959
TiO_2/Chit 0.33	5.71	4.25	0.22	0.11	0.962	0.971
TiO_2/Chit 0.65	4.34	3.33	0.13	0.11	0.982	0.946
TiO_2/Chit 1.33	2.70	1.92	0.11	0.08	0.903	0.978

nanocomposite containing the lowest TiO_2 had maximum q_m. This result was in accordance with the results of previous studies in which nanocomposite adsorption capacity was not affected by specific surface area but was influenced by the amount of free chitosan in the nanocomposite. The free OH and NH_2 groups in were not bound to TiO_2.

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 $OH^\bullet$ 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^- (≈ electron) and h^+ (≈ 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.

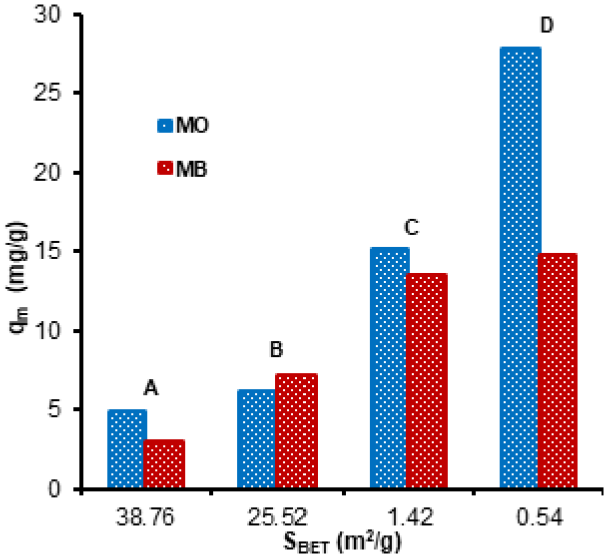

Fig 8. The relationship between specific surface area (S_{BET}) with maximum adsorption capacity (q_m) for MO and MB (Graph of A is TiO_2/Chit 1.3; B is TiO_2/Chit 0.65; C is TiO_2/Chit 0.33, and D is TiO_2/Chit 0.13)

The mechanism of photodegradation of MO and MB by TiO_2-nanocomposite chitosan under UV radiation as illustrated in Fig. 9 (adapted from Nawi

[15]). 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 ($-SO_3^-$) of MO molecule and protonated amine ($-NH_3^+$) of chitosan, while the adsorption of cationic dye (MB) occurred through electrostatic attraction between electrons of MB molecules in aromatic ring and $-NH_3^+$ group of chitosan. Adsorption of MB was weaker because of the repulsing force between positive charges from MB and $-NH_3^+$ in chitosan [16].

In the second phase, TiO_2 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 TiO_2 photocatalyst is:

$$TiO_2 + h\nu \rightarrow TiO^* + h^+_{(VB)} + e^-_{(CB)}$$

The $h^+_{(VB)}$ was reacted with aqueous and produced a strong OH radical:

$$h^+_{(VB)} + OH^- \rightarrow \bullet OH$$

$$h^+_{(VB)} + H_2O \rightarrow \bullet OH + H^+$$

Dye molecules adsorbed on the surface of TiO_2 nanocomposite could be oxidized:

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

$$MO/MB + \bullet OH \rightarrow \text{ oxidation product}^*$$

($^*CO_2$, H_2O and mineral)

In the third phase, h^+ on the surface of TiO_2 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:

$$MO_{ad}/MB_{ad} + h^+ \rightarrow MO_{ad}^{\bullet}/MB_{ad}^{\bullet} + H^+$$

$$MO_{ad}^{\bullet}/MB_{ad}^{\bullet} + TiO_2 \rightarrow MO_{ad}^{+}/MB_{ad}^{+} + TiO_2(e^-_{(CB)})$$

Meanwhile, $e^-_{(CB)}$ had reacted with dissolved oxygen (O_2) to produce OH, O_2^-, HO_2 or H_2O_2 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 TiO_2 weight in photodegradation process

Addition of the amount of TiO_2 in TiO_2-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 TiO_2 could

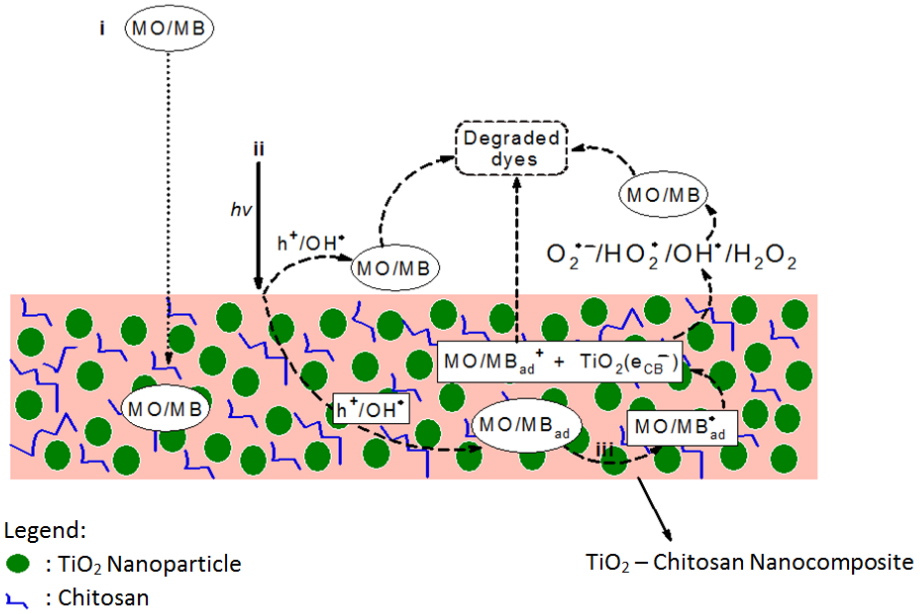

Fig 9. The hypothetical photodegradation mechanisms of MO and MB catalyzed by TiO_2-chitosan nanocomposite: (i) the adsorption of MO/MB on the photocatalyst nanocomposite surface, (II) direct degradation of MO/MB, which was adsorbed on the surface of the nanocomposite, by TiO_2 (III) the oxidation of MO/MB which was adsorbed on the chitosan surface, and the charge transfer from TiO_2 electron at the conduction band (e_{cb}^-)

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]:

$$r = -\frac{dC}{dt} = \frac{kK_L C_e}{1 + K_L C_e} = \ln\left(\frac{C_0}{C_e}\right) + K_L\left(C_0 - C_e\right) = kK_L\, t$$

r is the reaction rate, C_0 is the initial concentration, Ce is the concentration after t, with t represent the reaction time (min), K_L is the Langmuir adsorption constant, and

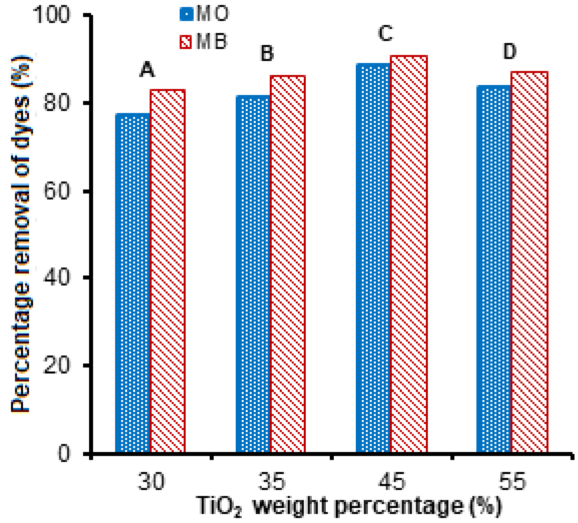

Fig 10. The effect of TiO_2 weight in nanocomposite to dye removal (Graph of A is TiO_2/Chit 0.13; B is TiO_2/ Chit 0.33; C is TiO_2/Chit 0.65; and D is TiO_2/Chit 1.3)

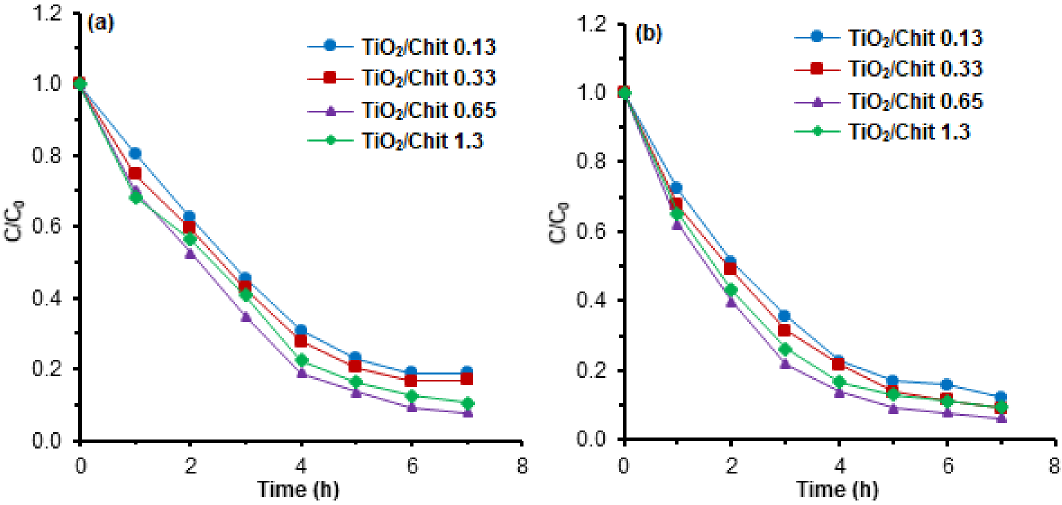

Fig 11. (a) Langmuir-Hinshelwood kinetic of MO photodegradation (b) Langmuir-Hinshelwood kinetic of MB photodegradation

k is the kinetic constant (min^{-1}). If K_LC_e <<; then $r = kK_LC_e$ 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:

$$-\ln\frac{C_e}{C_0}=k_{Obs}t$$

k_{Obs} was the observed kinetic constant (min^{-1}) and $k_{Obs} = kK_L$. The kinetic parameter of k_{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_{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 $k_{Obs} = k.K_L$ equation. The parameters of the observed kinetic constant rate (k_{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_{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_{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_{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

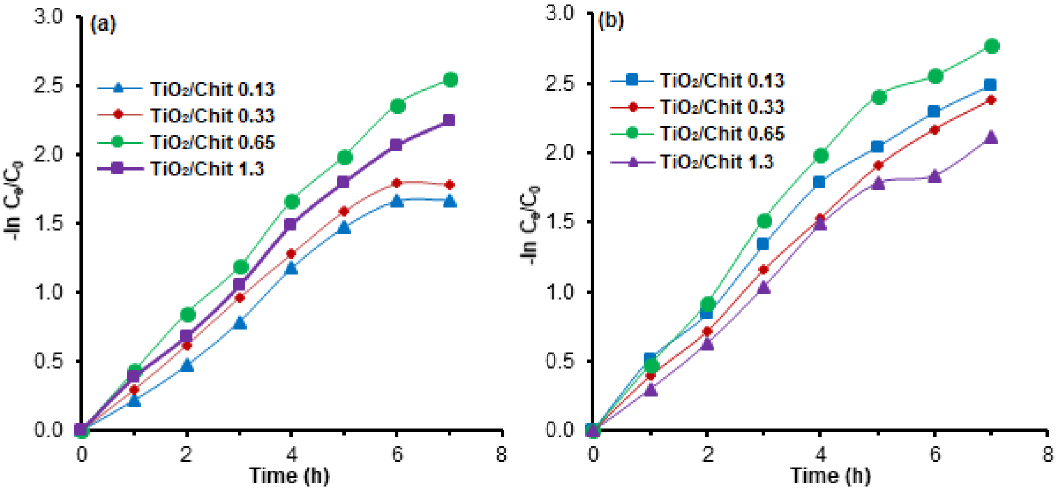

Fig 12. (a) Observed kinetic constant (k_{Obs}) of MO photodegradation follows the first order reaction (b) Observed kinetic constant (k_{Obs}) of MB photodegradation follows the first order reaction

Table 4. The photodegradation rate parameters of MO and MB catalyzed by TiO_2-chitosan nanocomposite

Nanocomposite	k_{Obs} (min^{-1})		K_L (L/Mg)		k (x 10^2 (min))	
Types	MO	MB	MO	MB	MO	MB
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

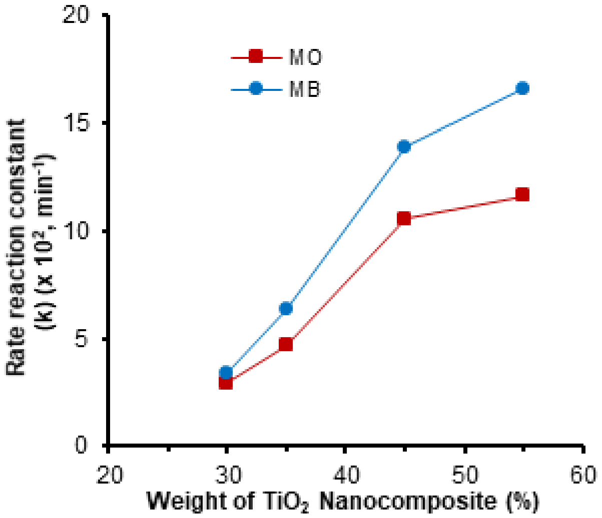

Fig 13. The relationship between TiO_2 weight with the kinetics (k) of MO and MB photodegradation

nanocomposites performance as a photocatalyst, because much more OH radicals had been able to increase photodegradation reactions.

The different kinetics in various levels of TiO_2 (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 (E_a) [22].

Two determining factors for the activation energy in nanocomposite were the weight of TiO_2 and the distribution of TiO_2 in the nanocomposite. Based on different energy activations in the nanocomposite, it was predicted that the distribution of TiO_2 in nanocomposite followed two types. First, TiO_2 was distributed closed in the chitosan matrix space. Second, TiO_2 was distributed inside and outside the chitosan matrix.

The first type occurred in the nanocomposites containing low TiO_2 weights, (as TiO_2/Chit 0.13 and TiO_2/Chit 0.33), while the second type occurred in the nanocomposite containing high TiO_2, (as in TiO_2 /Chit 0.65 and TiO_2/Chit 1.3). The distribution of TiO_2 inside and outside the chitosan matrix had a higher photodegradation than when TiO_2 was in the chitosan matrix. This result was confirmed by the increase in photodegradation reaction kinetic.

■ CONCLUSION

TiO_2-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 TiO_2 in nanocomposite was low due to higher amounts of -OH and -NH_2 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 TiO_2 nanocomposite.

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