Combination of photocatalytic degradation and adsorption in dye removal by TiO$_2$-chitosan-glycerol beads under natural sunlight

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Abstract. The synthesis of TiO$_2$-chitosan-glycerol (TiCsG) beads was prepared to determine the optimum condition for dye removal under natural sunlight. By using the orthogonal array design with five parameters (ratio of TiO$_2$/Chitosan, initial concentration of dyes, pH of solution, irradiation time, dose of TiCsG) to analyze their interaction such as well as optimizing the photocatalytic process. The significant parameters influent in the removal of Acid Blue 193, MO, NWY dyes were irradiation time ($p = 0.011$) and the ratio of TiO$_2$/chitosan ($p = 0.025$), while the initial concentration of dyes, pH of dye solution and dose of TiCsG were unimportant factors with $p > 0.05$. The optimum of factors based on the ratio of signal per noise to attain the highest dye removal ability of TiCsG was the percentage of TiO$_2$/chitosan = 2 % w/w (level 2), initial concentration of dye at level 5 (10 mg/L of AB 193, 5 mg/L for MO and 100 mg/L for NWY), pH =4.5 (level 2), irradiation time =1.5 h (level 5) and dose of TiCsG =0.2 g/mL (level 4).

Keywords: TiO$_2$, chitosan, glycerol, dye, Taguchi method

1. Introduction
Textile wastewater contains various dyes which are difficult to biological degrade due to their synthetic origin and complex aromatic molecular structures [1]. This poisonous waste effluent into the environment and damage human and aquatic life. Furthermore, colored wastewater can limit the penetration of sunlight and oxygen into the aquatic area [2]. Many approaches of dye treatment have been used, such as adsorption, sedimentation, chemicoagulation, biological methods, and advanced oxidation procedures. Adsorption is one of the acceptable physical methods for dye removal. Chitosan has been widely applied in textile wastewater treatment because of its high capacity on color and pollutant degradation [3, 4]. However, it is a high cost due to not reusable in general. The applications of photocatalysis have also received substantial attention in dye removal [5, 6]. Many photocatalysts such as TiO$_2$, ZnO, Fe$_2$O$_3$, WO$_3$, and Cu$_2$O were studied to degrade the contaminants under UV and visible radiation. Among those, TiO$_2$ has been the most concerned due to its relatively efficient, low price, non-toxic, chemically and biologically inert, and high photocatalytic activity under UV light irradiation [7]. The TiO$_2$ combining with chitosan can reduce the drawback of chitosan in regenerating the adsorbent. The functional groups of chitosan matrix captured dye. TiO$_2$ could degrade these adsorbed pollutants leading to the recovery of bio-sorbent chitosan [8]. Glycerol was added to stronger the
hydrogen bond in the chitosan matrix and increased the mechanical properties of chitosan [9]. Many research studied the ability of photocatalysis and adsorption, mechanism and kinetics of pollutant treatment, synergistic effects, and the TiO₂-chitosan characteristics [4, 10-12]. The dye degradation activities of TiO₂-chitosan-glycerol were significantly higher than that of TiO₂-chitosan [13].

In the present work, the synthesis of TiO₂-chitosan-glycerol beads was studied for dye removal under sunlight irradiation. Experimental factors for degradation of Methyl orange (MO), acid blue 193 (AB 193), and NearWash Yellow RCL (NWY), including dyes and photocatalyst concentrations, ratios of components in composite, pH, and irradiation time were investigated. The Taguchi method was used to investigate the optimum conditions and the correlation of factors for the dye removal ability, which was the target response variable.

2. Material and methods

2.1. Chemicals

High molecular weight chitosan was obtained from a company in Vietnam, degree of deacetylation was 91.6%. Commercial TiO₂ Degussa P25 (Merck, 80% anatase, 20% rutile) and glycerol (Merck, 99.5%) was used as a material for strengthening the mechanical properties of chitosan. Sodium triphosphate (TPP, China, > 98.0%) was used as solidifying chemical. Acid blue 193 (AB 193, Merck), methyl orange (MO, Merck), and Near Wash Yellow RCL (NWY, NearChimica) was chosen as dyes for analyzed the dye removal of TiCsG beads.

| Properties                         | Acid blue 193 (AB193) | Methyl orange (MO) | Near Wash Yellow (NWY) |
|------------------------------------|-----------------------|--------------------|------------------------|
| Molecular formula                  | C₄₀H₂₂CrN₄Na₂O₁₀S₂    | C₁₄H₁₂N₃NaO₃S     | C₂₄H₁₉ClF₁Na₂O₉S₂     |
| Molecular weight (g/mol)           | 880.7 g/mol           | 327.34 g/mol       | 742 g/mol              |
| Synonym                            |                       |                    |                        |
| Maximum absorbance values (nm)     | 598                   | 463                | 421                    |

2.2. Methods

Chitosan solution was prepared by dissolving in acetic acid 5% (v/v) solution. The ratio of the TiO₂ and glycerol was controlled at 1:10 (w/w) [13]. This mixture was poured into chitosan solution with various percentages of TiO₂ and chitosan from 1 to 5 (w/w). After that, this solution was stirred for 30 min. and homogenized by an ultrasonic device (Hielscher UP 100H) in 30 minutes to form TiO₂-chitosan-glycerol gel. This gel was added dropwise into the solution of TPP 1% (w/v) to form spherical particles.
The formed TiO$_2$-chitosan-glycerol beads were washed with distilled water and dried at 70°C for 8 h.

![Diagram of TiO$_2$/chitosan/glycerol bead formation process]

**Figure 1.** Procedure of TiCsG bead forming

### 2.3. Characterization

The crystal phase of the TiO$_2$-chitosan-glycerol beads was analyzed by X-ray diffraction (XRD) on a BRUKER D2-212917. Scanning Electron Microscope (FE SEMS-4800 Hitachi, Japan) was used to examine the materials' morphology. FT-IR spectra (Perkin-Elmer FT-IR) was used to assess the functional groups present in the TiCsG bead FT-IR.

### 2.4. Photocatalytic degradation experiments

The photocatalytic degradation of TiCsG was examined by taking three different dyes into glass tubes ($d = 2.0$ cm) under natural sunlight irradiation. The fixed amount of dyes (10-mL with specific material concentrations was axially conducted by shaker at noon with the sunlight intensity $> 30$ W/m$^2$).

After a fixed irradiated time, the sample was withdrawn and centrifuged to remove the minus material from the solution. The standard curve using UV visible spectrophotometer to analyze the dye concentration.

The dye removal efficiency (E%) of dyes was determined by the following equation (1):

$$E\% = \frac{(c_0-c)}{c_0} \times 100$$

where $C_0$ is the initial concentration of dye solution before photocatalysis and $C$ (mg/L) is the concentration of dye solution after a certain irradiation time.

### 2.5. Experimental design methodology

The orthogonal array was determined by the Taguchi approach to design several experiments and to analyze the quality through the signal-to-noise ratio (S/N). Five controllable factors included the percentage of TiO$_2$/chitosan, initial concentration of dye, pH of dye solution, irradiation time, and the dosage of TiCsG bead. The levels of initial dye concentration for AB, MO, and NWY dyes are $2-10$ mg/L, $1-5$ mg/L, and $20-100$ mg/L, respectively. The levels of initial dye concentration for AB, MO, and NWY dyes are a, b, c, d, and e, which are presented in table 3. The difference in initial dye concentration for AB 193, MO, and NWY is due to the dark color when changing the concentration. The experiments were designed to maximize the dye removal efficiency of TiO$_2$-chitosan-glycerol beads. According to the Taguchi approach, the number of experiments to analyze the factor effect of...
photocatalysis with 5 factors and 5 levels is 25. The statistical results using MINITAB software V16 based on the Taguchi method was done.

Table 2. Factors and their level was designed according to Taguchi approach.

| Independent factors       | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 |
|---------------------------|---------|---------|---------|---------|---------|
| TiO$_2$/chitosan % (w/w)  | A       | 1       | 2       | 3       | 4       | 5       |
| Initial concentration of dye (mg/L) | B       | a       | b       | c       | d       | e       |
| pH of dye solution        | C       | 3       | 4.5     | 6       | 7.5     | 9       |
| Irradiation time (hours)  | D       | 0.5     | 1       | 1.5     | 2       | 2.5     |
| TiCsG loading (g/mL)      | E       | 0.05    | 0.1     | 0.15    | 0.2     | 0.25    |
| TiCsG1 TiCsG2 TiCsG3 TiCsG4 TiCsG5 |

Table 3. The levels of initial dye concentration for AB, MO and NWY dyes applied for experimental design by Taguchi method

| Initial dye concentration | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 |
|---------------------------|---------|---------|---------|---------|---------|
| AB dye (mg/L)             | a       | b       | c       | d       | e       |
| MO dye (mg/L)             | 1       | 2       | 3       | 4       | 5       |
| NWY (mg/L)                | 20      | 40      | 60      | 80      | 100     |

3. Results and discussion

3.1. TiCsG bead characterization

Figure 2. X-ray diffraction patterns of chitosan beads and TiCsG (TiCsG 1- TiCsG 5) with various ratios of TiO$_2$ and chitosan (from 1 to 5%, w/w).

X-ray diffraction patterns of powder TiCsG with percentage ratios of TiO$_2$ and chitosan ranging from 1 to 5% (w/w) are shown in Figure 2. With the existence of TiO$_2$ in the matrix of TiCsG, the crystallographic structure of chitosan changed. The peaks of the amorphous state of chitosan in TiCsG...
patterns changed from 18.8° to 18.5°[13]. The X-ray diffraction pattern for anatase phase TiO$_2$ (1 1 0) gives single diffraction lines at 25.2, 37.6, 47.9, 53.9, 54.2, 62.5, and 74.9°. The intensity of these diffraction lines increased with the TiO$_2$ loading because the amorphous region increases in the chitosan matrix during the synthesis of material.

The shape and morphology of the TiCsG were presented in Figure 3. SEM analysis shows rough surface (Figure 3b) compared to chitosan beads (without TiO$_2$) (Figure 3a). The formation of minute granules is due to TiO$_2$ the aggregation (0.5 μm–5 μm in diameter) wrapped with chitosan [13]. The TiCsG beads are non-spherical form with the color of white-yellow and the mean diameter around 1mm.

The functional groups of chitosan and TiCsG (TiO$_2$/chitosan ratios varied from 1 to 5%, w/w) determined by FTIR spectra are presented in Figure 4. The strong band at 3382 cm$^{-1}$ can be correspond to the O-H and N-H stretching as the intramolecular hydrogen bonds in chitosan [14]. The signals at around 2976 and 2895 cm$^{-1}$ can be attributed to the stretching vibrations of C-H groups and asymmetric stretching, respectively [14]. The peaks at 1668 and 1383 cm$^{-1}$ assigned to residual N-acetyl groups including the amide-I band (C=O stretching) and CH$_2$ group (C-H bending) in chitosan, respectively.
The bands at 1090 and 1051 cm\(^{-1}\) belong to C-O stretching. The C-H bending out of monosaccharides was confirmed by the band at 881 cm\(^{-1}\) [15].

3.2. Taguchi approach to optimize the highest color degradation

A Taguchi approach with the L\(25\) orthogonal array design (25 test runs) was used to determine significant parameters and their intercorrelation for dye removal. Experiments were carried on under constant solar radiation (solar intensity > 30 W/cm\(^2\)). The results of 25 experiments for three dyes degradation are shown in Table 4. Experiments were performed in triplicate.

| Run no. | Factors | AB 193 removal efficiency (%) | MO removal efficiency (%) | NWY removal efficiency (%) |
|---------|---------|-------------------------------|--------------------------|---------------------------|
| TiO\(_2\)/chitosan, w/w | Initial concentration dye of (mg/L) | pH | Irradiation time (hour) | Dosage of TiCsG (g/mL) |  |  |
| 1 | 1 | 2 | 3.0 | 0.5 | 0.05 | 16.34 | 57.72 | 23.52 |
| 2 | 1 | 4 | 4.5 | 1.0 | 0.10 | 37.78 | 74.07 | 61.08 |
| 3 | 1 | 6 | 6.0 | 1.5 | 0.15 | 48.40 | 90.34 | 65.75 |
| 4 | 1 | 8 | 7.5 | 2.0 | 0.20 | 52.13 | 93.82 | 73.24 |
| 5 | 1 | 10 | 9.0 | 2.5 | 0.25 | 51.80 | 82.40 | 72.65 |
| 6 | 2 | 2 | 4.5 | 1.5 | 0.20 | 79.02 | 84.57 | 70.35 |
| 7 | 2 | 4 | 6.0 | 2.0 | 0.25 | 48.40 | 90.34 | 65.75 |
| 8 | 2 | 6 | 7.5 | 2.5 | 0.05 | 67.58 | 88.93 | 72.38 |
| 9 | 2 | 8 | 9.0 | 0.5 | 0.10 | 28.60 | 77.19 | 35.14 |
| 10 | 2 | 10 | 3.0 | 1.0 | 0.15 | 77.45 | 83.07 | 72.62 |
| 11 | 3 | 2 | 6.0 | 2.5 | 0.10 | 58.77 | 84.08 | 68.35 |
| 12 | 3 | 4 | 7.5 | 0.5 | 0.15 | 24.68 | 70.17 | 33.98 |
| 13 | 3 | 6 | 9.0 | 1.0 | 0.20 | 52.55 | 84.86 | 64.03 |
| 14 | 3 | 8 | 3.0 | 1.5 | 0.25 | 68.95 | 94.55 | 72.67 |
| 15 | 3 | 10 | 4.5 | 2.0 | 0.05 | 55.01 | 83.49 | 72.16 |
| 16 | 4 | 2 | 7.5 | 1.0 | 0.25 | 21.07 | 77.69 | 59.49 |
| 17 | 4 | 4 | 9.0 | 1.5 | 0.05 | 39.56 | 77.03 | 53.20 |
| 18 | 4 | 6 | 3.0 | 2.0 | 0.10 | 45.38 | 93.79 | 71.42 |
| 19 | 4 | 8 | 4.5 | 2.5 | 0.15 | 55.91 | 93.74 | 73.33 |
| 20 | 4 | 10 | 6.0 | 0.5 | 0.20 | 28.27 | 77.80 | 46.77 |
| 21 | 5 | 2 | 9.0 | 2.0 | 0.15 | 54.28 | 78.48 | 65.15 |
| 22 | 5 | 4 | 3.0 | 2.5 | 0.20 | 69.48 | 81.89 | 72.73 |
| 23 | 5 | 6 | 4.5 | 0.5 | 0.25 | 36.46 | 62.77 | 51.55 |
| 24 | 5 | 8 | 6.0 | 1.0 | 0.05 | 29.34 | 73.58 | 33.84 |
| 25 | 5 | 10 | 7.5 | 1.5 | 0.10 | 48.81 | 75.56 | 60.34 |

The analysis of variance (ANOVA) uses a general linear model to determine the influent of factors and their confidence levels. The p-value evaluated the significance of factors. The statistically significant test of factors was evaluated by the p-value ≤ 0.05 [16]. From the results in Table 5, the color degradation efficiencies of TiCsG were significantly affected by the irradiation time (p = 0.001 for MO,
p = 0.011 for AB 193 and p = 0.005 for NWY). The TiO$_2$/chitosan ratio was also an important parameter for AB 193 and MO dye, while the TiCsG loading was a significant factor for MO and NWY. The initial dye concentration and pH were insignificant factors with p > 0.05.

| Factors                              | AB 193 | MO   | NWY  |
|--------------------------------------|--------|------|------|
| TiO$_2$/chitosan ratio (% (w/w))     | 9.50   | 18.73| 0.64 |
| Initial concentration of dye (mg/L)  | 0.52   | 14.87| 1.4  |
| pH of dye solution                   | 2.03   | 2.83 | 2.01 |
| Irradiation time (hour)              | 14.86  | 57.53| 23.16|
| TiCsG loading (g/mL)                 | 2.87   | 9.87 | 7.16 |

The average removal percentages of dyes were analyzed using the MINITAB 19 software to evaluate the effect of each factor on the optimization criteria. Here, the output $S/N$ ratio from the analysis of variance (ANOVA) would be estimated for every experiment to determine the distinguishing characteristic between control or signal parameters. The ratio of $S/N$ for every results of experiments in the orthogonal array was chosen to be "the larger, the better" to get the maximum in the expected dye removal efficiencies of TiCsG. From this, control factors (significant effects on the signal to noise ratio) and signal factors (most minor effect on the $S/N$ ratio) were determined [17].

3.2.1. Effect of irradiation time

As can be seen in Figure 5, with 0.5 to 2.5 h of irradiation time, there was an extreme increase in $S/N$ ratio from 36.73 to 38.7 for MO, 31.32 to 36.71 for NWY, and 28.3 to 35.61 for AB 193, respectively. Obviously, the higher the photocatalytic time, the more interaction between the materials and the light energy to produce OH$^-$, and the interaction between dyes and the hydroxyl radicals [18]. Therefore, the efficiencies of dye removal were increased with the irradiation time. On the other hand, there are no significant differences in $S/N$ ratio more than 1.5 h illuminating because of the termination reaction that reduce the quantity of free radicals. Therefore, the optimum irradiation time for three dyes was 1.5 h. Under 1.5 h irradiation, the dye removal percentage of MO reached 84%, while that of AB 193 and NWY were 68 and 63%, respectively.
3.2.2. Effect of TiO$_2$/chitosan

Figure 6. The effect of the percentage of TiO$_2$ and Chitosan on the dyes degradation.

The amount of catalyst amount could be positive and negative influent on the photodegradation rate [19]. The percentage of TiO$_2$/chitosan was tested with different concentrations in the range 1 – 5 % (w/w). Figure 6 show that the S/N of TiO$_2$/chitosan ratio for AB 193 fluctuated while those for other dyes were stable. The S/N increased when the dosage of TiO$_2$/chitosan increased to the optimum point of 2 % (w/w) and then reduced at higher values. Other researchers [20, 21] also found the same results. The initial efficiencies were directly proportional to catalyst concentration due to increasing TiO$_2$ and, consequently, the number of photons adsorbed. However, with the excessive amounts of catalysts, the aggregation of TiO$_2$ particles leads to a decreased number of active sites. Furthermore, the opacity of beads limits the penetration of light when the excess catalyst was mixed [19, 20]. Thus, an optimum amount of catalyst should be mixed to ensure the absorption of light photons for efficient photomineralization [22].

3.2.3. Effect of TiCsG loading

Figure 7. The effect of TiCsG loading on the dyes degradation.

The interaction of TiCsG bead on the dye removal efficiencies was determined by S/N ratio, and the results are illustrated in Figure 7. The increase in the mass of material from 0.05 to 0.2 g/mL led to an increase in the ratio of S/N and then reduced with 0.25 g TiCsG per mL. The highest S/N of TiCsG for MO, AB 193 and NWY were 34.51, 38.53 and 36.2, respectively, with 0.2 g/mL. The higher the adsorbent dose (chitosan), the higher surface area and the more functional groups of chitosan,
consequently leading to higher dye removal. Nonetheless, an excessive quantity of chitosan (0.2 g/mL) reduced the dye removal of TiCsG beads. The downtrend of S/N ratio showed that the conglomeration and interaction of chitosan and TiO₂ particles resulting from a high dose of TiCsG beads [22]. Therefore, the optimum amount of TiCsG beads was fixed at 0.2 g/mL based on the largest S/N ratio and minimum material mass. The dye degradation efficiency of TiCsG at the optimum loading was 84.6% for MO, while that for AB 193 and NWY was only 68.8% and 65.4%, respectively. These results could be explained by that AB 193 and NWY formula have double (SO₃Na) group compared to MO, making MO be degraded faster.

3.2.4. Effect of pH

Figure 8. The effect of pH on the S/N ratio for dyes degradation.

The pH of dye solution plays a significant role in adsorption and photocatalysis. According to the S/N ratio analyzed from test runs with various pH in range 3 to 9, the strong dependence of pH on dye removal abilities of AB 193 and NWY while a bit of influence on MO dye degradation. At low pH, the presence of appropriate quantities of protons protonates the amino groups of chitosan molecules to formed NH₃⁺ and changes TiCsG bead to positive charge, consequently [23]. Furthermore, it is noted that the dyes have negatively charged sulfonic groups in acidic conditions. Therefore, these groups could be adsorbed by TiCsG beads [24]. On the other hand, with the pH value less than pH_{pzc} of TiO₂ Degussa P25 (pH_{pzc} = 6.5) [25], the surface of TiO₂ particles gain a positive charge (TiOH⁺) and also attracted negative dye more and faster.

\[
\begin{align*}
\text{Dye} - \text{SO}_3\text{Na} + \text{H}_2\text{O} \rightarrow & \text{Dye} - \text{SO}_3^- + \text{Na}^+ \\
\text{Adsorbent} - \text{NH}_2^- + \text{H}^+ (\text{acid condition}) \rightarrow & \text{Adsorbent} - \text{NH}_3^+ \\
\text{Adsorbent} - \text{NH}_3^+ + \text{Dye} - \text{SO}_3^- \rightarrow & \text{Adsorbent} - \text{NH}_3^+ - \text{O}_3\text{S} - \text{Dye}
\end{align*}
\]

3.2.5. Effect of initial dye concentration

As shown in Figure 9, the ratio of S/N increased with increasing the initial dye concentration up to level 4 with MO dye and level 3 with AB 193 and NWY dye and then slightly declined. These results agree with other studies [27-29]. The higher the initial concentration of dye, the more the driving force of the concentration gradient. However, the limit of dye adsorption per unit of chitosan molecule would reduce at high dye concentration. Furthermore, the more initial concentration of dye, the more color intensity. Therefore, the dye molecules are adsorbed on the surface of the adsorbent, and dye molecules absorb UV irradiation rather than TiCsG beads [27]. The color intensity reduced the penetration of light passing through the chitosan medium to reach the catalyst's surface [30]. This leads to less photon's energy reaching the active sites on the catalyst, resulting in the number of hydroxyl radicals produced.
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Figure 9. The effect of initial dye concentration on the S/N ratio for dyes degradation.

From all the effect of factors, the optimum of parameters based on the S/N ratio to attain the highest dye removal ability of TiCsG was the percentage of TiO$_2$/chitosan = 2 \% w/w (level 2), initial dye concentration = 10 mg/L of AB 193, 5 mg/L for MO and 100 mg/L for NWY (level 5), pH = 4.5 (level 2), irradiation time = 1.5 h (level 3) and dose of TiCsG = 0.2 g/mL (level 4). However, the obtained results showed that the effects of these factors on MO and NWY degradation efficiency were not so significant. The molecular formula of MO has just one SO$_3$ group while that of NWY has two. This could make higher efficiency on dye removal of MO than NWY. In addition, molecular formula of AB 193 with Cr$^{3+}$ is more complicate to degrade with the composite. Therefore, the optimum of factors depends on AB 193.

4. Conclusions

The photocatalytic efficiency of TiCsG under natural sunlight was investigated for degradation of three different dyes (methyl orange, acid blue 193 and Near Wash Yellow). A Taguchi approach using the orthogonal array experimental design was carried out to optimize the factors affecting the photocatalytic efficiency of CS/PVA/TiO$_2$ nanocomposite included: ratio of TiO$_2$/chitosan, initial concentration of dye, pH, irradiation time, and dose of TiCsG. The optimum conditions were found from the statistical results of L25 test runs: TiO$_2$/chitosan = 2 \% w/w, initial dye concentration = 10 mg/L of AB 193, 5 mg/L for MO and 100 mg/L for NWY, pH = 4.5, irradiation time = 1.5 h and dose of TiCsG. The time irradiation was the most significant factor for the dye removal ability of AB 193 and MO dye, followed by the percentage of TiO$_2$/chitosan. The initial concentration dye and pH were unimportant factors with $p > 0.05$. The combination of TiO$_2$ and chitosan in dye removal offers the potential to reduce the drawback of chitosan in regenerating the adsorbent. The results of TiCsG under natural sunlight show the effective ability of this combination in textile wastewater treatment.

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