Engineering Chemistry
ISSN: 2813-6535, Vol. 11, pp 25-38
doi:10.4028/p-yjgnY5

Submitted: 2024-12-21
Revised: 2025-04-28
Accepted: 2025-05-05
Online: 2025-09-10

Fabrication of Silica-Modified Green Mussel Shell-Based Chitosan Hydrogel Bio-Composite and Xanthan Gum from Tofu Dregs as Methylene Blue Photodegradator

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Keywords: Chitosan, Methylene Blue, Photodegradation, Silica, Xanthan Gum.

Abstract. Methylene Blue (MB) waste is damaging to both humans and the environment. Chitosan is one of the MB adsorbents that may be made from green mussel shells. Because CS compounds have a limited adsorption capacity for MB, a restricted surface area, and poor chemical stability, thus necessitating modification. CS/XG was created by combining the three chemicals silica (SiO_2), tofu pulp, and the anionic substance Xanthan Gum (XG). SiO_2 hydrogel bio-composite with the aid of UV light, can absorb MB by photodegradation. The objective of this paper is to analyze the regeneration and photocatalysis kinetics based on the kinetic rate constant of the bio-composite photodegradation, and to identify the ideal circumstances of MB photodegradation by CS/XG.SiO_2 hydrogel bio-composite with Box-Behnken design. The CS/XG bio-composite was synthesized from chitosan (green mussel shell waste) and xanthan gum (tofu dregs waste) with added SiO_2 to adsorb methylene blue via photodegradation. The use of green mussel shells and tofu dregs is significant as it turns abundant waste into valuable materials, reducing pollution and supporting low-cost, eco-friendly wastewater treatment.The variables were pH, MB concentration, and photodegradation time. The results showed that the optimum condition occurred at pH 9.43; MB concentration 5.054 ppm; and irradiation time 119.67 minutes with % degradation of 94.2%. After the 5th reuse of CS/XG.SiO_2, the % degradation only decreased from 94.2% to 79.4%, indicating good regeneration ability. Analysis of photodegradation kinetics showed accurate modelling using the Modified Elovich model with an R^2 value of 0.9805 and a photodegradation kinetic rate constant of 0.0010 min^{-1}.

Introduction

The growth of the modern industrial sector has resulted in the increased use of dyes that are harmful to the environment. Methylene Blue (MB) is one of the cationic dyes widely used in industry today. Long-term exposure to methylene blue is reported to have negative impacts on health and the environment [1]. Therefore, removing this pollutant from waters is important for the environment. A material with a large adsorbing capacity to MB is chitosan (CS). Chitosan can be obtained through deacetylation of chitin compounds found in the shells of arthropods such as green mussels (Perna viridis L) because they contain 20.62% chitosan [2]. Chitosan has an adsorption capacity of 18.47 mg/g at alkaline pH [3] so it has the potential to be an adsorbent raw material. However, chitosan has several disadvantages, namely low chemical stability, low surface area, and small adsorption capacity for methylene blue. Modifications are needed to chitosan to adsorb larger amounts of methylene blue [4], such as the addition of anionic compound Xanthan Gum (XG). The

electrostatic interaction between the anionic groups of XG and the cationic groups of methylene blue can promote a stronger bond between the dye molecules and the composite material [4]. However, the addition of XG compound is not ideal to optimise the degradation ability of chitosan so that a photocatalyst material such as SiO2 is needed to increase the surface area of the composite. The chosen degradation method is the photodegradation method due to low chemical usage, low operational costs, easy operation, and can be used repeatedly [5]. This is supported by previous research, the use of SiO_2 can degrade methylene blue perfectly for 90 seconds by photodegradation [6]. The combination of the three materials CS/XG.SiO_2 produces bio-composite materials that are effective in photodegradation of cationic textile dye waste such as methylene blue. There has been no previous research using chitosan from shellfish and xanthan gum from tofu dregs for MB photodegradation.

In this study, CS/XG bio-composite was synthesised. SiO2 with chitosan from green mussel shell waste and Xanthan Gum from tofu pulp waste that can adsorb methylene blue by photodegradation. Previous research synthesised similar composite materials but used commercial chitosan and Xanthan Gum. The dye used in the previous study was methyl orange and the usual degradation method. Other studies also synthesised chitosan from green mussel shells and Xanthan Gum from tofu pulp separately without being combined into one material and without being used to adsorb methylene blue. This is the novelty of this research.

The variables in this study are pH, time, and methylene blue concentration using statistical analysis of variable optimisation, namely multivariable Box-Behnken Design with three independent variables. In addition, we synthesised chitosan from green mussel shells and Xanthan Gum based on tofu pulp in the manufacture of CS/XG.SiO_2 adsorbent. Finally, we conducted regeneration tests and analysed the photodegradation kinetics activity. The problem in this research is what is the optimum condition of methylene blue photodegradation using CS/XG.SiO_2 bio-composite and how is the regeneration ability and kinetic activity of photocatalysis based on the kinetic rate constant of CS/XG.SiO_2 bio-composite photodegradation. The purpose of this research is to determine the optimum condition of methylene blue photodegradation using CS/XG.SiO_2 bio-composite by Box-Behnken Design method and analyse the regeneration and photocatalysis kinetics of CS/XG.SiO_2 bio-composite photodegradation.

Research Methods

Materials

The tools used in this research are glass beaker, thermometer, magnetic stirrer, glass stirrer, hotplate, three neck flask, oven, filter paper, erlenmeyer, ultrasonic homogenizer BLIH-301, N4S UV-Vis spectrophotometer, autoclave, fed batch fermentor, centrifuge, and Vivaria 7 Watt UVC lamp. Meanwhile, the materials used in this research are wet tofu pulp obtained from a tofu factory in Surabaya, green mussel shells from the coast of Kenjeran Beach Surabaya, distilled water, deionised water, tetraethyl orthosilicate (TEOS) Merck, ammonium hydroxide (NH_4OH), acetone, acetic acid (CH_3COOH), ethanol, methylene blue, HCl solution, NaOH, filter paper, sucrose, citric acid, glutamic acid, KH_2PO_4, trace elements, and isolate *Xanthomonas campestris* bacteria.

Research Variables

The independent variables used in this study are pH (3-11), time (30-120 minutes), and methylene blue concentration (5-20 ppm) based on Box-behnken design analysis using Design Expert V11 software; the control variables are synthesis operating conditions, temperature, adsorbent composition and mass, test stirring speed, and UV light source; and the dependent variable is methylene blue catalytic photodegradation efficiency.

Research Procedure

The flow diagram of this research shown below.

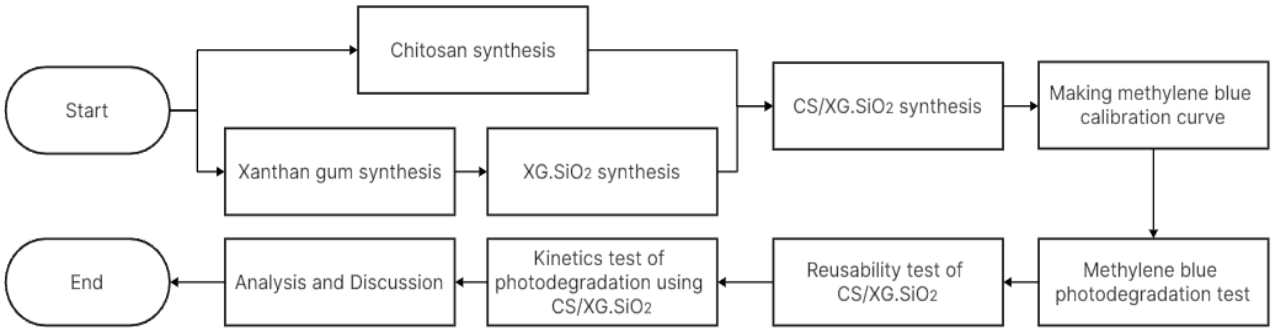


Fig. 1. Flow Diagram of The Research

Synthesis of Chitosan from Green Mussel Shells

Chitosan synthesis has been carried out based on previous research by Firyanto [7]. Chitosan was synthesised from green mussel shells (*Perna viridis*) through three processes, namely deproteination, demineralisation, and deacetylation. In the deproteination process, the crushed green mussel shells were added with 1 N NaOH in the ratio of 1:10 (w/v), stirred with a stirrer at 500 rpm, and heated at 90 oC for 90 minutes. The deproteinated sample was then rinsed with distilled water, filtered, and oven dried for 2 hours. Next, the dried samples were demineralised with 1 N HCl in a ratio of 1:10 (w/v) and stirred with a stirrer at 70 oC with a speed of 500 rpm for 60 minutes. The demineralised samples were rinsed with distilled water, filtered, and oven dried for 2 hours. The process ended with deacetylation of chitin with 25% w/v NaOH solution in the ratio of 1:10 (w/v) into the dry demineralised sample and stirred with a 400 rpm stirrer at 90°C for 90 minutes. The remaining solid was rinsed with distilled water, filtered, and oven dried for 2 hours.

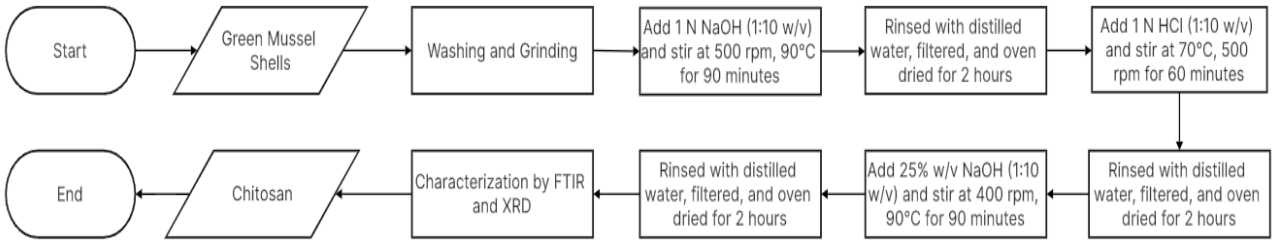


Fig. 2. Flow Diagram of Chitosan Synthesis from Green Mussel Shells

Xanthan Gum Synthesis Using Tofu Dregs

Xanthan Gum synthesis has been carried out based on previous research by Gustiani et al. (2018). Wet tofu dregs were dried using an oven at 65 ºC and made a sterile tofu dregs solution with a concentration of 2% (w/v). Then, inoculation of *Xanthomonas campestris* bacteria was carried out on Nutrient Broth (NB) liquid media for 24 hours. From the liquid media, 20% (v/v) of the media will be taken to be mixed into the sterile tofu pulp solution along with 1% (w/v) sucrose, 5 g/L citric acid, 2.5 g/L glutamic acid, 0.5 g/L KH_2PO_4, and 0.04 g/L trace elements. Then, fermentation was carried out for 5 days under batch conditions with a temperature of 28ºC. After that, the fermentation results were dried using an oven at 105ºC for 3 hours.

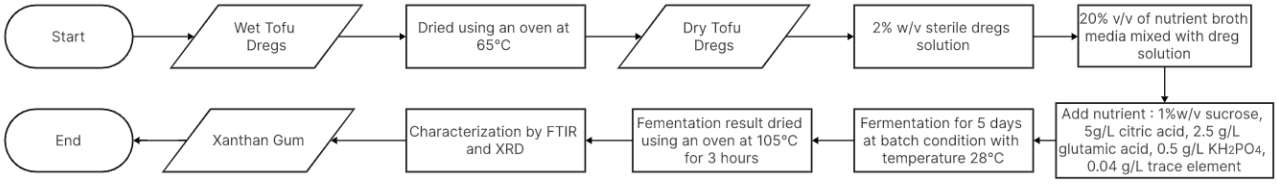


Fig. 3. Flow Diagram of Xanthan Gum Synthesis from Tofu Dregs

Synthesis of XG.SiO_2 Composite

The synthesis of XG.SiO_2 composite was carried out based on previous research by Rahmatpour [4]. The first stage prepared Xanthan Gum solution consisting of 50 mg of Xanthan Gum powder and 20 mL of distilled water in beaker A and stirred at 25°C for 6 hours. In beaker B, 4 mL of ethanol and 1.5 mL of tetraethyl orthosilicate (TEOS) were dissolved. Meanwhile, in beaker C, 1 mL of 14.7 N ammonium hydroxide solution was prepared. Then, the solutions in beakers A, B, and C were mixed in a round bottom flask and the reaction was carried out at 70°C for 5 hours in an N_2 gas environment. Then, 50 mL of acetone was added and the resulting sample was filtered. After that, the sample was dried in an oven at 60°C for 24 hours and a white powder XG.SiO_2 was obtained.

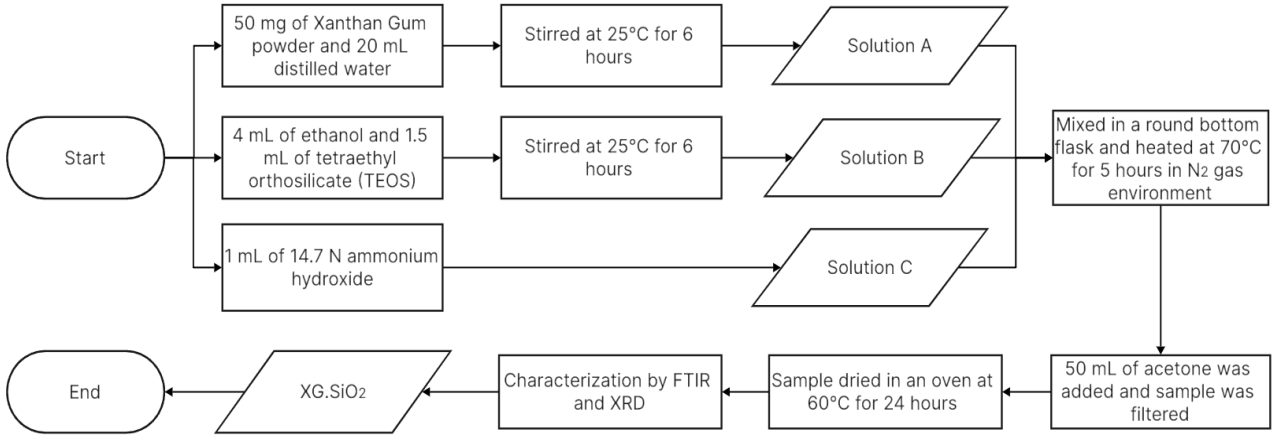


Fig. 4. Flow Diagram of XG.SiO_2 Synthesis

Synthesis of CS/XG.SiO_2 Composite

The synthesis of CS/XG.SiO_2 composite was made with 0.4 g chitosan dissolved in 32 mL of 2% v/v acetic acid solution and stirred until a clear viscous solution was obtained. In a separate erlenmeyer, 57 mg of XG.SiO_2 was mixed in 8 mL of deionised water and homogenised with an ultrasonic homogenizer for 30 minutes. Then, the XG.SiO_2 suspension was added to the chitosan solution while stirring for 1 hour at 40°C. The hydrogels formed were dehydrated by soaking in 30 mL of ethanol for 24 hours with three ethanol changes. After that, the hydrogels were dried in an oven at 50°C for 24 hours.

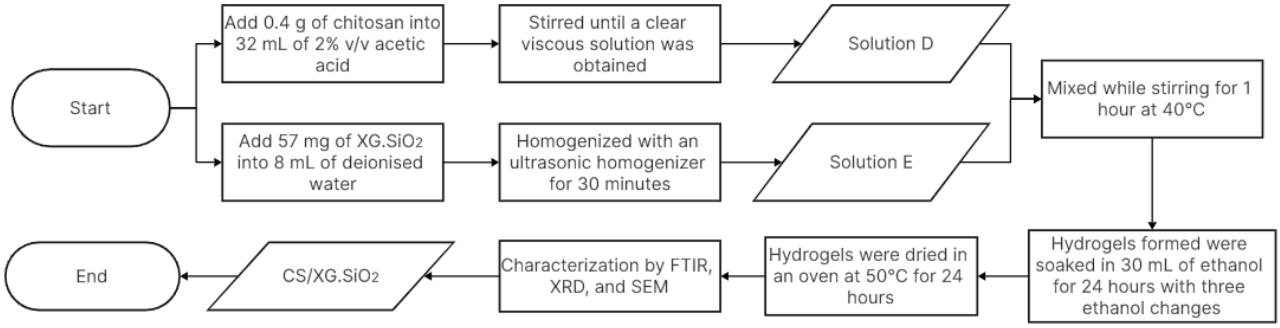


Fig. 5. Flow Diagram of CS/XG.SiO_2 Synthesis

Characterisation of Synthesised Materials

Characterisation of the synthesised CS/XG.SiO_2 composite was carried out using FTIR, XRD, and SEM tests. FTIR was conducted to determine the functional groups of the composite. XRD to determine the crystal structure in the composite and its crystallinity. Meanwhile, SEM aims to determine the surface morphology of composites. For each of the synthesised compounds, namely chitosan, Xanthan Gum, and XG.SiO_2, FTIR and XRD characterisation were also carried out to determine the success of the compound synthesis.

Methylene Blue Photodegradation Test

The photodegradation test was conducted by preparing 100 mL of Methylene Blue (MB) solution with a concentration of 5-20 ppm. Then, 50 mg of composite was put into the solution at room temperature accompanied by a 200 rpm stirrer in the dark room for 20 minutes until it reached adsorption equilibrium. Then, irradiation was carried out by a 7 Watt UVC lamp for an irradiation time of 30-120 minutes and a solution pH of 3-11 according to each run. The following is an illustration of photodegradation testing.

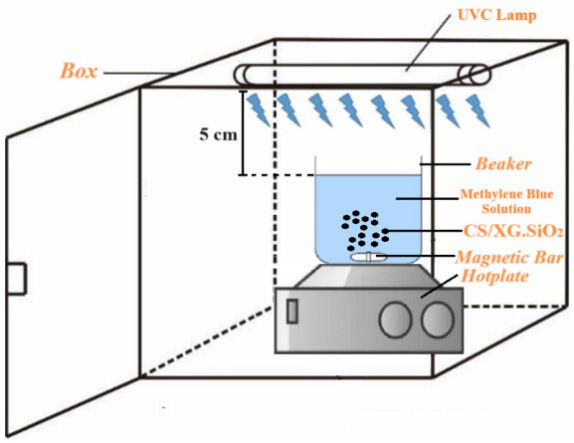


Fig. 6. Illustration of Photodegradation Testing

After irradiation, the composite was separated by centrifugation at 1500 rpm for 5 min and the remaining MB concentration was calculated by absorbance with a UV-Vis spectrophotometer at a wavelength of 668 nm. The % degradation was calculated based on the following formula.

$$\%\ Degradation = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

With C_0 and C_t being the initial and final MB concentrations, respectively. Data analysis using Design Expert v11 software with statistical analysis of Box-Behnken polynomial design quadratic model with the following equation.

$$R = Y_0 + Y_1A + Y_2B + Y_3C + Y_12AB + Y_13AC + \cdots \quad (2)$$

With R is the response (% degradation), Y is the factor coefficient, and A, B, and C are the independent variable factors. The equation obtained is then used to predict the optimum condition of % degradation of multiple independent variables. The Box-Behnken factor design in this study is as follows.

Table 1. Range and Level of Independent Variables in Box-Behnken Design

Design Variable	Factor	Unit	Coded Level		
			-1	0	1
A	pH	-	3.00	7.00	11.00
B	MB Concetration	ppm	5	12.5	20
C	Time	minute	30.00	75.00	120.00

Reusability Test of Chitosan/XG.SiO_2 as Methylene Blue Photodegradation

The reusability test was carried out by experimenting at the optimum conditions obtained based on the previous analysis. The composite that has been separated with filter paper was desorbed with 10% v/v HNO_3 solution. Then, the desorbed composite was reused up to five times and the % photodegradation was analysed at each repetition.

Photocatalysis Kinetics Test of Chitosan/XG.SiO_2

Photocatalysis kinetics test was conducted to test the photocatalytic activity of the composite. This was done by setting up photodegradation testing at optimum conditions and taking aliquots at every interval of 20 minutes to 120 minutes. Then, the calculation of MB concentration at each time and analysis of photocatalysis kinetics using several models, namely Order 0, 1, 2, and modified Elovich respectively with the following mathematical equations.

Table 2. Mathematical Equation of Kinetics Model

No.	Model	Kinetics Formula	Reference
1	0 Order	$\frac{dCt}{dt} = -k_{photo}$	Luo (2019)
2	1st Order	$\frac{dCt}{dt} = -k_{photo} \times Ct$	Luo (2019)
3	2nd Order	$\frac{dCt}{dt} = -k_{photo} \times Ct^2$	Luo (2019)
4	*Modified* Elovich	$\frac{dCt}{dt} = -k_{photo} \times Co \times \exp(\beta(\ Ct - Co\ ))$	Luo (2019)

Result and Discussion

Material Synthesis

Chitosan was synthesised from green mussel shell waste with three stages, namely deproteination (protein removal), demineralisation (mineral dissolution), and deacetylation (removal of acetyl groups) with the final result in Figure 7.a. The resulting chitosan is white and smooth and has a % yield per stage, namely proteination, demineralisation, and deacetylation of 61.29%; 40.57%; and 90.64% w/w of green mussel shells with an overall yield of 22.54% w/w and obtained % Deacetylation (DD) for chitosan of 87.8%, indicating good chitosan quality (%DD > 70%) [8].

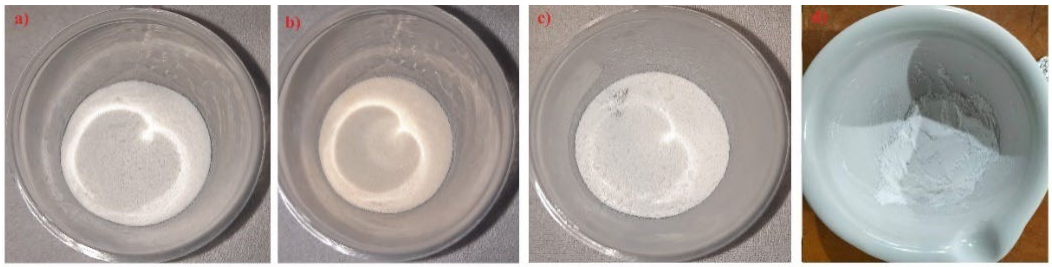


Fig. 7. Material Synthesis Results: a. Chitosan(CS), b. *Xanthan Gum*, c. XG.SiO_2, dan d. CS/XG.SiO_2

Furthermore, Xanthan Gum was synthesised from tofu pulp waste using the help of Xanthomonas campestris bacteria with the results in Figure 7.b. Xanthan gum was beige in colour and smooth and obtained a % yield w/w of 19.22% of the mass of dry tofu pulp used as fermentation media. After Xanthan Gum powder is obtained, the next step is to synthesise XG.SiO_2 using the Stober method with an alkaline atmosphere. XG.SiO_2 that has been synthesised can be seen in Figure 7.c and obtained a yield of 10.06% w/w of the mass of Xanthan Gum and tetraethyl orthosilicate (TEOS) used. CS/XG.SiO_2 as the last material that became the adsorbent was synthesised by forming a composite of chitosan and XG.SiO_2 with the results as shown in Figure 7.d obtained a yield of 50.06% w/w of the mass of chitosan and XG.SiO_2 used.

Characterization of Materials

The following are the results of the FTIR and XRD spectra of the synthesised material.

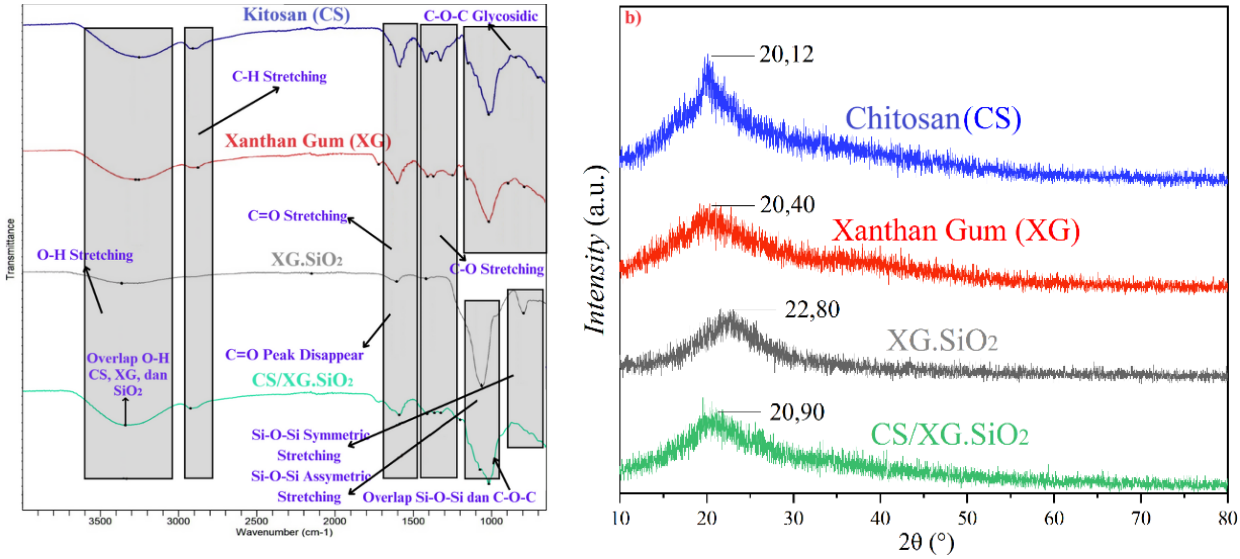


Fig. 8. FTIR Spectrum (a) and XRD Spectrum (b) of Citosan (CS), *Xanthan Gum* (XG), XG.SiO_2, dan CS/ XG.SiO_2 Synthetised

Figure 8.a shows the FTIR spectra of synthesised chitosan (CS), Xanthan Gum (XG), XG.SiO_2 , and CS/XG.SiO_2. The peaks at 3100-3600; 2900-2964; 1600-1700; 1240-1420 cm^{-1} are due to the presence of O-H stretching, C-H stretching, C=O stretching, and C-O stretching vibrations in the four materials, respectively. In the FTIR spectra of chitosan and Xanthan Gum, there is a peak at 842.4 - 700.7 cm^{-1} in the form of C-O-C vibrations which indicates the presence of asymmetric glycosidic bonds between N-acetylglucosamine and D-glucosamine monomers in chitosan polymers (Pang, 2024) and the presence of glycosidic bonds between glucose monomers and glucuronic acid in Xanthan Gum. The FTIR spectrum of XG.SiO_2 showed peaks at 1060 cm^{-1} and 792.1 cm^{-1} indicating the vibrations of Si-O-Si assymetric stretching and Si-O-Si symetric stretching groups. The missing peak at 1710.5 cm^{-1} which was previously in Xanthan Gum indicates that Xanthan Gum is involved

in the formation of mesoporous silica (SiO2) [4]. In addition, there are peaks at 1019.4 and 1075.3 cm^{-1} which are the overlap of Si-O-Si in silica and C-O-C in chitosan and Xanthan Gum. The peak at 1590-1650 cm-1 shows the overlap of amide group in chitosan and carboxyl anion group in Xanthan Gum due to the combination of $-NH^{3+}$ and $-CO2^{-}$. Broadened peak at 3000-3600 cm^{-1} due to the combination of O-H, N-H, and Si-O-H stretching indicates the presence of intermolecular hydrogen bonds in CS/XG.SiO_2 [4].

Figure 3.b shows the XRD spectra of the synthesised chitosan (CS), Xanthan Gum (XG) and XG.SiO_2. Chitosan shows a broadened peak at 2θ = 20.12 which indicates the attribution of semi-crystalline polysaccharides. Xanthan gum also shows a broadened peak at 2θ = 20.4 which indicates similar to chitosan. Meanwhile, XG.SiO_2 showed a broadened peak at 2θ = 22.3; slightly larger than the 2θ value of Xanthan Gum. This peak indicates the presence of mesoporous SiO2 and looks widened which indicates that the mesoporous SiO2 formed is included in the amorphous compound [4]. The following is an analysis of the crystallinity of the synthesised material.

Tabel 3. Crystallinity of Material Synthesised Based on XRD Data

Material	*Crystal Area*	*Amorphous Area*	*Crystallinity (%)*
CS	12821.67	24051.30	53.31
XG	10282.84	19732.50	52.11
XG.SiO_2	7485.83	13945.26	53.68
CS/XG.SiO_2	8488.42	18475.42	45.94

Table 3 shows that CS/XG.SiO_2experienced a reduction in crystallinity to 45.94% compared to chitosan (CS), Xanthan Gum (XG), and XG.SiO_2. This means that CS/XG.SiO_2 has an increasingly amorphous and porous form so that the surface area is getting bigger and has a positive impact on MB adsorption.

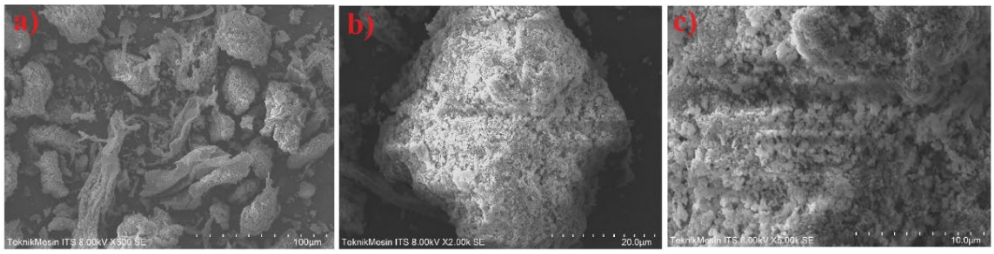
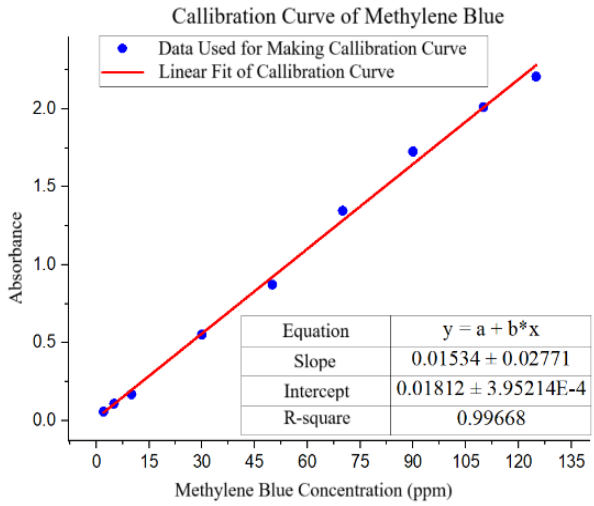


Fig. 9. Scanning Electron Microscopy Result of CS/XG.SiO_2 at various magnifications a) 500x, b) 2000x, dan c) 5000x.

After all materials were tested with FTIR and XRD, CS/XG.SiO_2 adsorbent was tested with SEM to see the morphology or surface of the material. Figure 9 shows the results of SEM testing of CS/XG.SiO_2 adsorbent at various magnifications. At 5000x magnification (Figure 9.c), it can be seen that the surface of the synthesised CS/XG.SiO_2 has a rough and porous surface and does not show a shape with a separate phase. This indicates that CS and XG/SiO2 are suitable if combined into a single material into a hydrogel. In addition, the thickened layer shows that there is a coupling interaction between chitosan and XG.SiO_2 [4].

Testing Photodegradation Ability of CS/XG.SiO_2

Here is the methylene blue calibration curve at maximum wavelength (λ_{maks}) nya (668 nm) to determine the concentration of methylene blue before and after the test.



Analysis of Variance (ANOVA)

	Sum of Squares	*Mean Square*	*F Value*	*P Value*
Model	5.70167	5.70167	2103	<0.0001
Error	0.01898	0.00271		
Total	5.72065			

Summary

Intercept		*Slope*		*Statistics*
Value	*Standard Error*	*Value*	*Standard Error*	*Adj. R-Square*
0.01534	0.02771	0.01812	3.95214E-4	0.99621

Statistics

Residual Sum of Squares	0.01898
Pearson's r	0.99834
R-Square (COD)	0.99668
Adj. R-Square	0.99621

Fig. 10. Calibration Curve of Methylene Blue at λ = 668 nm

Based on Figure 10, the equation of the calibration straight line is A = 0.01812 C + 0.01534 with a value of R^2 curve is 0.99668 which is close to the value of one and the P-value <0.0001 which indicates that the correlation value is very good so that the curve is accurate in predicting the MB concentration value before and after the test.

Variable testing was based on the Box-Behnken statistical method of three variables, namely pH (A), MB concentration (B) in ppm, and time (C) in minutes consisting of 15 runs with the following experimental % photodegradation results.

Table 4. Photodegradation Testing Results with Box-Behnken Design

Run	Coded Level of Variables			Experimental Variables			% Degradation
	A	B	C	A	B	C	
1	1	0	-1	11	12,5	30	60,3
2	0	1	1	7	20	120	73,5
3	0	0	0	7	12,5	75	53,3
4	-1	1	0	3	20	75	9,7
5	1	-1	0	11	5	75	73,2
6	0	-1	-1	7	5	30	51,6
7	1	1	0	11	20	75	63,0
8	0	0	0	7	12,5	75	55,2
9	0	0	0	7	12,5	75	51,6
10	-1	-1	0	3	5	75	10,9
11	-1	0	-1	3	12,5	30	8,1
12	1	0	1	11	12,5	120	71,1
13	0	1	-1	7	20	30	42,3
14	0	-1	1	7	5	120	89,0
15	-1	0	1	3	12,5	120	16,0

Analysis of Variance (ANOVA), Residual, dan *Prediction* Model

Statistical analyses were performed using Design Expert v11 software. ANOVA study was conducted on the developed model to determine the significance of the main factors affecting the response rate of the photocatalytic process and the results are presented in Table 4. The most suitable model is with R^2 and predicted R^2 values close to one, namely the quadratic model, with A, B, and C are linear factors, A^2, B^2, and C^2 are quadratic factors, and AB, AC, BC are A-B, A-C, and B-C interaction factors, respectively.

Table 5. ANOVA Analysis of Quadratic Model Experiments

Source	*F-value*	*P-value*	*Significance*	R^2	*Predicted* R^2
Model	230.84	< 0.0001	*Significant*		
A	1455.78	< 0.0001	*Significant*		
B	11.59	0.0192	*Significant*		
C	103.61	0.0002	*Significant*		
AB	0.0952	0.7701	*Not significant*	0.9976	0.9648
AC	14.43	0.0127	*Significant*		
BC	0.0041	0.9515	*Not significant*		
A^2	466.07	< 0.0001	*Significant*		
B^2	2.35	0.1855	*Not significant*		
C^2	6.27	0.0542	*Not significant*		
Lack of Fit	6.08	0.1445	*Not significant*		

Specifically, the F-value and P-value were used to determine the significance of each coefficient of the developed mathematical model. The F-value and P-value of the model were calculated to be 230.84 and <0.0001, respectively. This implies that the independent variables used in the modelling are significant for the modelling of methylene blue photodegradation by CS/XG.SiO_2. P-value < 0.05 indicates that the factor used is significant. In this case, the linear factors A, B, and C, the quadratic factor A^2, and the interaction AC were significant for the modelling of MB photodegradation. Whereas, the factors AB, BC, B^2, and C^2 are not significant enough but necessary to determine the relationship between independent variables. The large P-value of Lack of Fit, 0.1445 (>0.05) indicates that there is no significant evidence to reject the null hypothesis, indicating that the model fits the data. This is also consistent with the residual analysis and model predictions as follows.

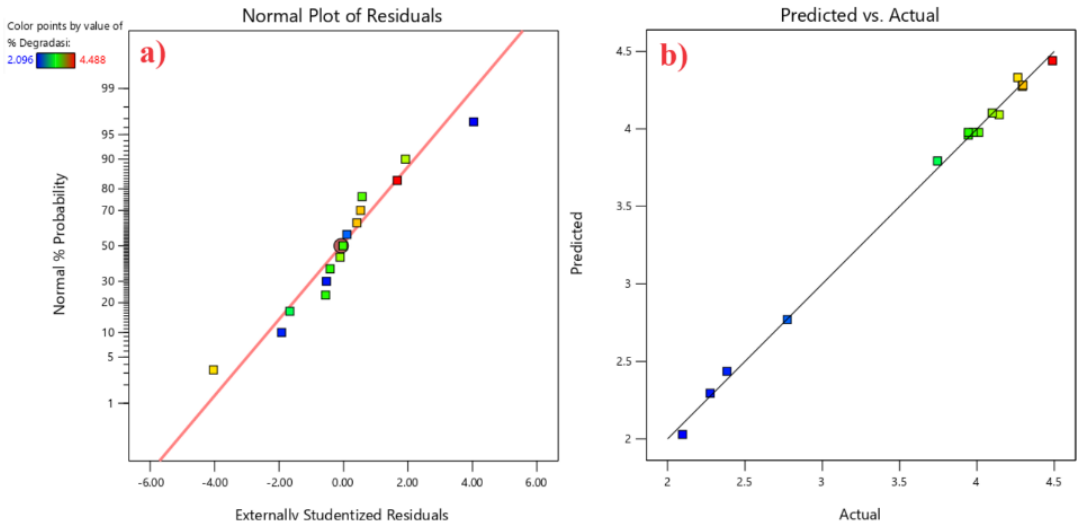


Fig. 11. Graphs a. Normal Plot of Residuals and b. Predicted vs Actual Data

Based on Figure 11.a, it is found that the residual values are normally distributed around a straight line and in Figure 11.b, the predicted values are distributed close to the actual values so that the data obtained are valid and the prediction model can be used. In addition, the prediction R^2 value is 0.9648 which shows the model is accurate in predicting the results. The final equation of the Box-Behnken design quadratic model obtained is as follows.

$$\%\ \boldsymbol{Degradation} = 3.98 + 0{,}909A - 0{,}081B + 0{,}2424C - 0{,}0104AB - 0{,}1279AC + 0{,}002BC - 0{,}76A^2 + 0{,}054B^2 + 0{,}0878C^2 \quad (3)$$

Effect of Free Variables on % Degradation of Methylene Blue

Analysis of the effect of the variables pH, methylene blue concentration, and irradiation time was carried out using 3D surface response graphs plotted to determine the effect of experimental variables on the response as follows.

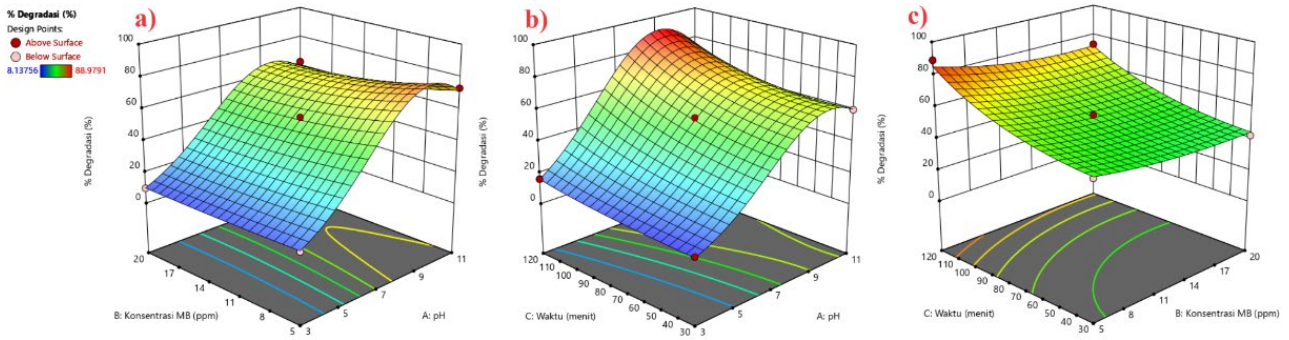


Fig. 12. 3D Surface Response Graph of Interaction Between Two Variables on Methylene Blue Photodegradation

Figure 12.a shows the effect of pH and initial concentration of methylene blue on the percentage degradation of methylene blue. The degradation efficiency gradually increased from pH 3 to pH 10 and finally decreased from pH 10 to pH 11 at constant MB concentration. This is because the surface charge of CS/XG.SiO_2 adsorbent depends on the protonation and deprotonation of functional groups so that changes in pH can change the surface charge. The MB removal rate is maximum in the red coloured region, precisely at pH around 10. This is due to the weak electrostatic attraction between the negative groups of the dye and the positive groups of the adsorbent at higher pH levels (7-10). When the pH exceeds 10, the OH concentration gradually increases and OH and MB become increasingly competing for binding to the CS/XG.SiO_2 surface, thus reducing MB interaction and degradation efficiency [4].

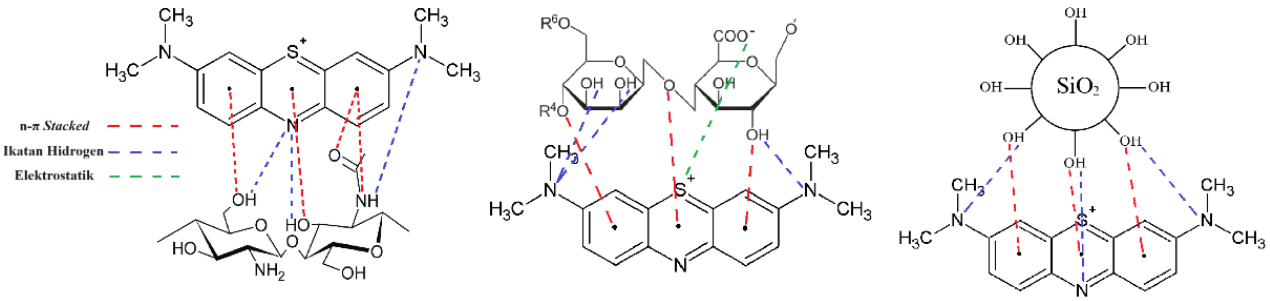


Fig. 13. Interaction of CS/XG.SiO_2 with Methylene Blue

At constant pH, the photodegradation efficiency increased with the increase of irradiation time with an optimum condition of 120 minutes as shown in Figure 12.b This is because the longer the irradiation time, the more energy received by CS/XG.SiO_2 degrade methylene blue. Whereas, at constant time, the photodegradation efficiency first increases when the MB concentration is lower

until a peak and finally decreases when the MB concentration is higher. As shown in Figure 12.c, the optimum state is at 5 ppm MB. When MB is present at a low concentration, the active sites of the adsorbent are empty and sufficient to adsorb a large number of dye molecules. However, at high initial MB concentrations, the number of fixed active sites becomes easily filled, making MB photodegradation more difficult [4].

Free Variable Optimisation with Box-Behnken Design

Optimisation of the independent variables was carried out using the previously calculated mathematical model equations to obtain the point with the highest % degradation. The following is an analysis of determining the point with three optimum variables.

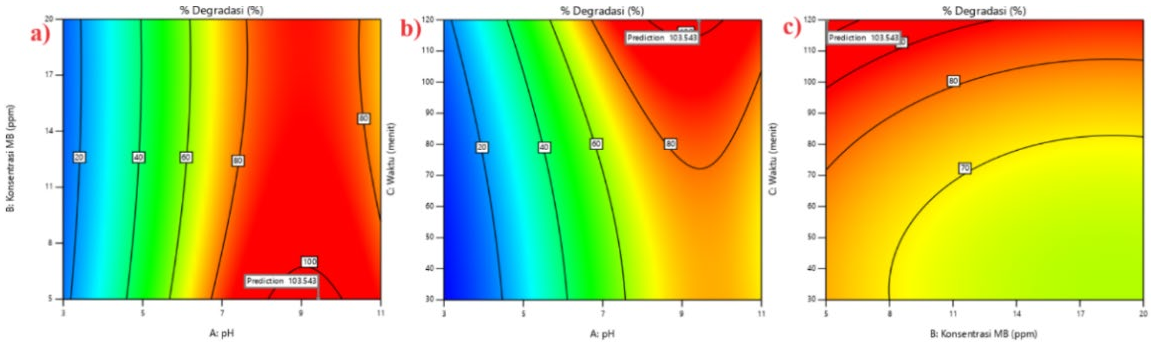


Fig. 14. 2D Graph of Free Variable Optimisation Determination

Based on Box-Behnken design analysis, the point with optimum % degradation is located at the centre of the red colour, precisely at pH = 9.43; MB concentration = 5.054 ppm, and irradiation time of 119.67 minutes with a predicted % degradation of 103.5%. After experimentation with the optimum variables, the % degradation was 94.2%. These results confirm the validity of the mathematical model of photodegradation of the synthesised CS/XG.SiO_2 material.

Reusability Analysis of CS/XG.SiO_2

Reusability analysis is used to test the reuse of CS/XG.SiO_2. The following is a graph of CS/XG.SiO_2 reusability.

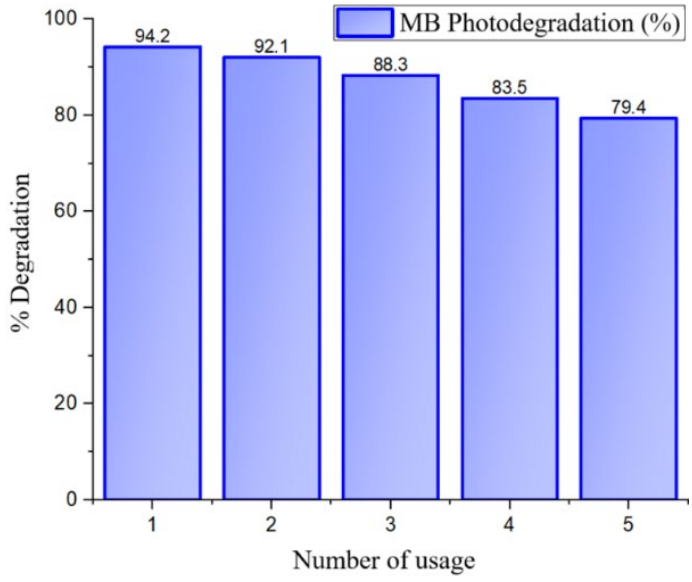


Fig. 15. Graph of % MB Degradation on Reuse of CS/XG.SiO2

Based on Figure 15, after the 5th reuse of CS/XG.SiO_2 the percent degradation only decreased from 94.2% to 79.4% which indicates CS/XG.SiO_2 is effective when used repeatedly.

Analysis of MB Photodegradation Kinetics with CS/XG.SiO_2

The kinetics of methylene blue photodegradation with CS/XG.SiO_2 was conducted to obtain the rate constant value of methylene blue photodegradation. In this study, four commonly used kinetic models namely order 0, 1, 2, and modified Elovich were investigated using data generated from experimental processes at optimum conditions after Box-Behnken optimisation.

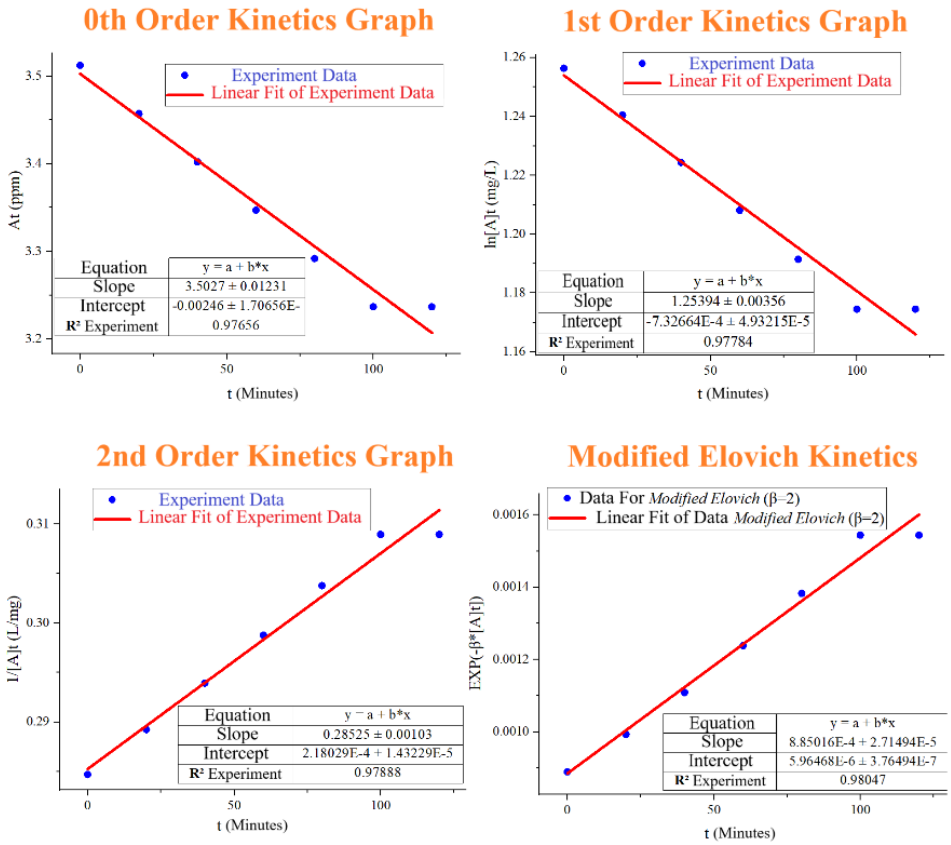


Fig. 16. Model Graph of Photodegradation Kinetics of MB with CS/XG.SiO_2

With parameter values for each kinetics model as follows.

Table 6. Parameter Values of Each MB Photodegradation Kinetics Model

Kinetics Model	Parameter	Value	Kinetics Model	Parameter	Value
0 Order	k (ppm.minute)	0,0025	**1st Order**	k (/minute)	0,0007
	$[A]_0$ Calc. (ppm)	3,5027		$[A]_0$ Calc. (ppm)	3,5041
	$[A]_0$ Exp. (ppm)	3,5126		$[A]_0$ Exp. (ppm)	3,5126
	R^2	0,9766		R^2	0,9778
2nd Order	k (L/mg.minute)	0,0002	***Modified Elovich*** **(β = 2)**	k (/minute)	0,0010
	$[A]_0$ Calc. (ppm)	3,5057		$[A]_0$ Calc. (ppm)	3,5150
	$[A]_0$ Exp. (ppm)	3,5126		$[A]_0$ Exp. (ppm)	3,5126
	R^2	0,9789		R^2	0,9805

Of the four models, the closest R^2 value model to one is the Modified Elovich model, which is 0.9805 which shows a very good correlation in the photodegradation of methylene blue by CS/XG.SiO_2. This indicates that the methylene blue removal process consists of chemical adsorption and photodegradation processes that run synergistically [9]. The photodegradation rate constant value based on the Modified Elovich model is 0.0010/min.

Summary

CS/XG.SiO_2 hydrogel bio-composite has been successfully synthesised by combining chitosan (CS) compounds from green mussel shells (Perna viridis) and Xanthan Gum Silica (XG.SiO_2) as shown by the results of FTIR, XRD, and SEM characterisation. The results showed that the optimum condition of photodegradation occurred at pH 9.43; MB concentration of 5.054 ppm; and UV irradiation time for 119.67 minutes. Under the optimum conditions, the % degradation was 94.2%. After the 5th reuse of CS/XG.SiO_2, the %degradation only decreased from 94.2% to 79.4%, indicating that CS/XG.SiO_2 was effectively used repeatedly. The photodegradation kinetic rate constant value was 0.0010 min^{-1} based on the Modified Elovich model with R^2 0.9805. These findings highlight the strong potential of the CS/XG.SiO_2 hydrogel bio-composite for real-world applications, particularly in the treatment of textile wastewater containing dye pollutants. For future research, scaling up the synthesis process and exploring the use of visible light sources for photodegradation are recommended to further enhance the practicality and sustainability of this material in industrial settings.

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