ALCHEMY Jurnal Penelitian Kimia

Official Website: https://jurnal.uns.ac.id/alchemy

ISSN 1412-4092
EISSN 2443-4183

Synthesis of Silica Aerogel from Rice Husk Modified Trimethylchlorosilane (TMCS) as an Adsorbent for Methylene Blue

Dyah Setyaningrum*, Erwanto Erwanto, Dian Khoirun Nisya'

Department of Chemistry, Faculty of Science and Engineering, Bojonegoro University
Jalan Lettu Suyitno No.2, Glendeng, Kalirejo, Bojonegoro, Jawa Timur 62119 Indonesia

Corresponding author: dyah_kimia@unigoro.ac.id

DOI: 10.20961/alchemy.22.2.112186.371-380

Received 12 July 2026, Revised 4 September 2026, Accepted 11 September 2026, Published 30 September 2026

Keywords:

adsorption;
aerogel;
methylene blue;
rice husk;
trimethylchlorosilane (TMCS).

ABSTRACT. This study investigated the synthesis and silylation of biomass-derived silica aerogels from rice husk ash for methylene blue (MB) adsorption under ambient-pressure drying (APD). Surface modification was conducted using trimethylchlorosilane (TMCS) in an ethanol/n-hexane co-solvent system to prevent capillary-induced pore collapse. The optimal silylation ratio (1:2:1 of silica:TMCS:n-hexane) yielded a superhydrophobic aerogel with a water contact angle of 152°, specific surface area of 795 m^2/g, pore volume of 5.75 cm^3/g, and 97.8% porosity. Fourier transform infrared (FTIR) spectroscopy confirmed successful surface modification, as evidenced by the appearance of Si–O–CH_3 (962 cm^{-1}) and –$Si(CH_3)_3$ (2950 cm^{-1}) peaks, while X-ray diffraction (XRD) verified the preserved amorphous silica framework with a broad peak at $2\theta = 22°$. The optimized aerogel achieved maximum MB removal efficiency of 97.9% within 70 min (C_0 20 ppm) and an equilibrium capacity of 14.03 mg/g at 60 ppm. Non-linear modeling revealed that the adsorption was best described by pseudo-second-order kinetics (R^2=0.9935) and the Langmuir isotherm (R^2=0.9845), confirming a homogeneous, monolayer chemisorption mechanism.

INTRODUCTION

Silica aerogel is a lightweight, nanoporous material formed by replacing the liquid phase within the silica gel structure with air. Owing to its unique microstructural properties, such as low density ranging between 3 and 500 mg/cm³ (Kaya and Deveci, 2020). Silica aerogel exhibits high porosity (80 – 99.8%), a large specific surface area (up to 1000 m^2/g), and colloidal particle sizes ranging from 2 to 60 nm, with pore sizes typically distributed between 1 and 100 nm (Feng *et al.*, 2018). Furthermore, their thermal conductivity can be as low as 0.013 W/(m·K) (Liu *et al.*, 2022). Silica aerogels have gained significant attraction for advanced thermal insulation, catalytic, adsorption, and environmental remediation (Li *et al.*, 2022; Liu *et al.*, 2022; Bangi *et al.*, 2024). Traditionally, silica aerogels are synthesized utilizing synthetic silicon alkoxide precursors, such as tetraethyl orthosilicate (TEOS) or tetramethyl orthosilicate (TMOS); however, these precursors are costly, toxic, and raise environmental concerns (Pisal and Rao, 2016; Len *et al.*, 2021; Andini *et al.*, 2022).

To resolve these precursor issues, biomass waste has emerged as an attractive alternative silica source. Rice husk is an abundant agricultural byproduct with a high silica content (90 – 98%), making it a promising raw material for silica-based products (Halim *et al.*, 2024). Converting this biomass waste into high-value materials not only reduces costs but also promotes sustainable waste management.

Silica aerogel derived from rice husk can be synthesized using the APD method, a more economical alternative to the expensive and hazardous supercritical drying technique (Halim *et al.*, 2024). Under APD conditions, high capillary stress at the liquid-gas meniscus during solvent evaporation can lead to structural shrinkage and network collapse into a dense xerogel. Successful synthesis requires careful solvent exchange and surface modifications to strengthen the silica gel network, reduce capillary stress, and preserve porosity.

Surface modification (silylation) represents a critical step for enhancing hydrophobicity and preventing structural collapse (Khedkar *et al.*, 2020). Several organosilane agents, such as dimethyldichlorosilane (DMDCS),

Cite this as: Setyaningrum, D., Erwanto, E., and Nisya', D. K. (2026). Synthesis of Silica Aerogel from Rice Husk Modified Trimethylchlorosilane (TMCS) as an Adsorbent for Methylene Blue. *ALCHEMY Jurnal Penelitian Kimia*, 22(2), 371-380. doi: https://dx.doi.org/10.20961/alchemy.22.2.112186.371-380.

Copyright © 2026, Universitas Sebelas Maret, ISSN 1412-4092, e ISSN 2443-4183

methyltrimethoxysilane (MTMS), and TMCS, were compared; the results showed that TMCS was the most effective silane agent. When introduced in a co-solvent system of ethanol and n-hexane, TMCS undergoes hydrolysis to form reactive silylated species that chemically substitute polar, hydrophilic surface silanol groups (≡Si–OH) with non-polar, low-surface-energy trimethylsilyl groups (–Si(CH_3)$_3$). This chemical conversion minimizes capillary stress and prevents adjacent pore walls from undergoing irreversible condensation reactions

Research on rice-husk-derived silica aerogels further highlights the influence of TMCS concentration on textural and surface properties. Feng *et al.* (2018) reported an optimal surface area of 945 m²/g, with an average pore size of 3.8 nm and a contact angle of 138.5°. Similarly, Mahardhika and Muldarisnur (2021) reported successful silylation, evidenced by the formation of $OSiCH_3$ groups, with increased hydrophobicity, as indicated by contact angles up to 92.5°, and morphological variations observed in SEM analysis. Additionally, Hidayatulloh *et al.* (2021) demonstrated that silica derived from rice husk possesses high porosity, abundant silanol and siloxane groups, and strong potential as an aerogel adsorbent for metal removal from water.

Despite advancements, past studies have often viewed silylation and environmental adsorption separately. This research focuses on rice husk-based silica aerogel modified with TMCS via a low-cost silylation method and examines how varying TMCS concentrations influence methylene blue adsorption. The adsorption mechanism was analyzed using kinetic models. The study highlights a sustainable approach to transforming agricultural waste into an effective wastewater adsorbent.

RESEARCH METHODS

Materials and Precursor Preparation

Rice husks used in this study were collected from local farmers in Bojonegoro, East Java. Standard sample handling protocols, including the use of gloves and protective polyester barriers, were implemented during collection to prevent external organic or inorganic contamination. All chemical reagents, such as TMCS (Sigma Aldrich, >98%), n-hexane as the non-polar solvent (Merck, >99%), ethanol as the co-solvent (Fisher Chemical, >99.9%), hydrochloric acid (HCl, Merck, 37%), sodium hydroxide (NaOH pellets, Sigma Aldrich >98%), deionized water, and MB (Sigma Aldrich, 99%), were of analytical grade and used without further purification.

Weight measurements were conducted using an analytical balance (JA3003 electronic balance), and thermal treatments were performed with a muffle furnace (B-One Mini Muffle Furnace 1210). A mortar and pestle, Herma glass beakers, and Mohr pipettes (Iwaki CTE33, Asashi Glass, Indonesia) were employed for sample handling and preparation. Mixing processes were facilitated using a magnetic stirrer (Cimarec). A suction ball (D&N, Germany), spatula, 100-mesh sieve, and Whatman filter paper were also used during sample preparation.

Silica aerogel was synthesized from rice husk ash as the precursor for sodium silicate using the sol-gel method (Figure 1), following Halim et al. (2016) and Ren et al. (2022), with modifications including varying the TMCS ratios and using HCl instead of CH_3COOH.

Extraction of Amorphous Silica and Hydrogel Synthesis

Rice husks were calcined at 600 °C for 4 h to remove organic matter and produce silica rice husk ash (RHA). To extract sodium silicate, 6 g of RHA was mixed with 90 mL of 1 M NaOH while heated at 120 °C for 24 h. The resulting sodium silicate solution was filtered under vacuum to separate any insoluble residues, yielding a clear sol. The silicate sol was treated with controlled dropwise addition of 1.5 M HCl under continuous magnetic stirring until gelation occurred (pH 5). The resulting silica gel was aged at room temperature for 24 h to promote polycondensation and mechanically strengthen the silica network.



Figure 1. Synthesis silica aerogel (a) RH extract sample, (b) Addition of NaOH, (c) The hydrogel, (d) Aging process, (e) Silica aerogel.

Copyright © 2026, Universitas Sebelas Maret, ISSN 1412-4092, e ISSN 2443-4183

Surface Modification and Ambient Drying

The aged hydrogel was immersed in deionized water for 12 h to remove residual salts (NaCl). The purified hydrogel underwent solvent exchange by immersion in ethanol at room temperature for 24 h, yielding a stable alcogel. The research variable was the volume of TMCS used as the silylating agent. Alcogel:TMCS:n-hexane ratios (v/v/v) of 1:0:1, 1:½:1, 1:1:1, 1:1½:1, and 1:2:1 were tested. The volumes of alcogel and n-hexane were held constant at 1 mL respectively, while TMCS was varied from 0 to 2 mL. The silylated wet gels were recovered via vacuum filtration. The modified gel was isolated via vacuum filtration and dried at 60 °C and 100 °C for 2 h.

Test and Characterization

The structural, textural, and surface modification properties of the synthesized aerogels were characterized. The crystalline structure of the silica aerogel was analyzed using X-ray diffraction (XRD, PANalytical X'Pert Pro). Chemical functional groups and the attachment of silylation were verified using Fourier transform infrared (FTIR) spectroscopy. The specific surface area, pore volume, and porosity were calculated via nitrogen adsorption-desorption isotherm using the BET method to evaluate network preservation. The physical surface hydrophobicity of the aerogel was quantified via static Water Contact Angle.

Adsorption performance toward MB was evaluated at room temperature. Concentrations of MB during kinetic and isotherm studies were determined using a UV-Vis spectrophotometer. Absorbance profiles of the concentration were measured at a maximum absorption wavelength.

Adsorption Studies

The adsorption performance of the silica aerogel was evaluated using a 25 mL solution containing 20 ppm MB and 0.1 g of aerogel. The mixture was stirred at 200 rpm, and samples were collected at 10, 30, 50, 70, and 90 minutes. Filtration was done using Whatman No. 42 filter paper, and the residual MB concentration was measured with a UV-Vis spectrophotometer at 665 nm (Usgodaarachchi *et al.*, 2021). After determining the optimum time, further tests were conducted at initial concentrations of 20, 30, 40, 50, and 60 ppm, following the same procedure. The adsorption capacity (q_e) and removal efficiency (R%) were calculated using Equations 1 and 2, respectively.

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

$$R(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where, $C_0 - C_e$ (mg/L) = the initial and equilibrium concentrations of MB, respectively. The volume of the aqueous solution used in the adsorption experiment is V (L), and the mass of the samples used is W (g).

Analyzing isotherm data is essential for developing equations that accurately represent adsorption results for design applications. The adsorption behavior can be modeled through several relationships, notably the Langmuir and the Freundlich isotherms. The Langmuir model assumes monolayer sorption on a homogeneous surface, with no interactions between adsorbed ions. The linear representation of the Langmuir equation is given in Equation 3.

$$\frac{C_e}{Q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (3)$$

On the other hand, the Freundlich isotherm describes non-ideal, heterogeneous adsorption. This equation is presented as Equation 4.

$$\log Q_e = \log Kf + \frac{1}{n} \log C_e \quad (4)$$

where, C_e (mg/L) denotes the adsorbate concentration at equilibrium, Q_e (mg/g) signifies the amount of adsorbate adsorbed at equilibrium per unit mass of adsorbent, K_L (L/mg) is Langmuir constant related to the capacity for adsorption, q_m (mg/g) represents the practical maximum adsorption capacity, Kf (mg/g) indicates the Freundlich adsorption capacity. $\frac{1}{n}$ reflects adsorption intensity.

RESULTS AND DISCUSSION

The synthesis and physicochemical evaluation of biomass-derived silica aerogels for environmental remediation represent a complex process-structure-performance. In this study, high-purity amorphous silica extracted from agricultural rice husk ash (RHA) was successfully synthesized into a nanoporous network and modified with trimethylchlorosilane (TMCS) under ambient-pressure drying (APD) conditions. The following

Copyright © 2026, Universitas Sebelas Maret, ISSN 1412-4092, e ISSN 2443-4183

sections systematically evaluate the chemical reaction mechanism, textural characteristics, physical hydrophobicity, phase structure, and dye adsorption performance toward methylene blue (MB).

Sol-Gel Synthesis and Silylation Mechanism

The synthesis of silica aerogel from rice husk ash (RHA) derived from biomass sol-gel transition, followed by wet-gel surface silylation (Figures 2 and 3). Titrating the precursor with hydrochloric acid (HCl), sodium silicate undergoes hydrolysis to form monomeric silicic acid ($Si(OH)_4$) (Reaction 1), which subsequently condenses to establish a highly cross-linked siloxane (≡Si–O–Si≡) hydrogel network (Reaction 2) (Karamikamkar *et al.*, 2020).

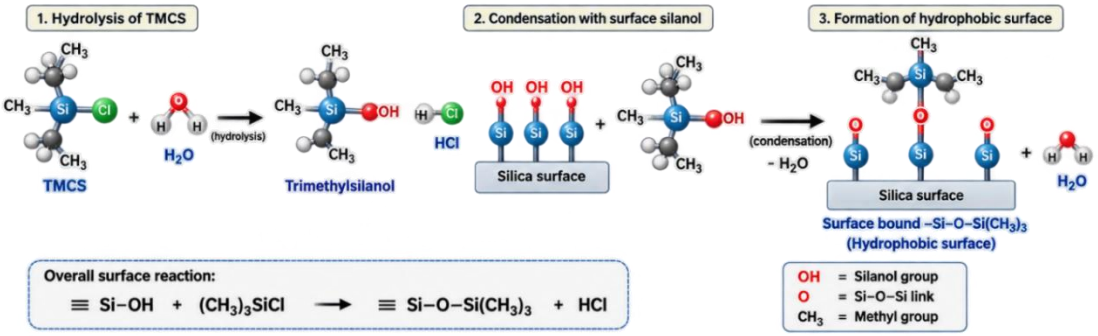


Figure 2. Mechanism of TMCS reaction with silica surface.

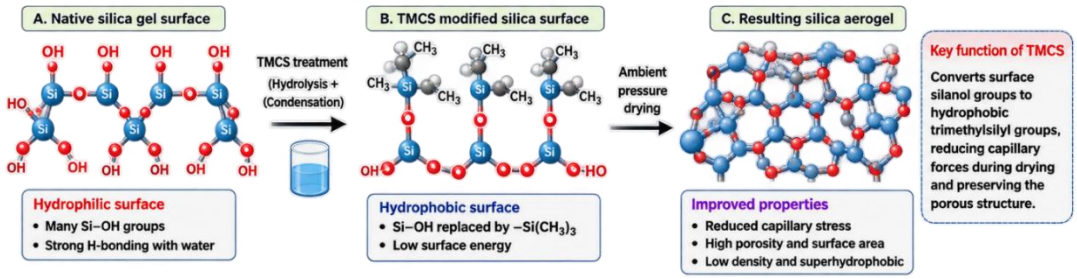


Figure 3. Process and effect of varying TMCS percentage on silica aerogel.

$$Na_2SiO_{3\,(aq)} + 2HCl_{\,(aq)} + H_2O_{\,(l)} \rightarrow Si(OH)_{4\,(aq)} + 2NaCl_{\,(aq)} \quad \text{(Reaction 1)}$$

$$Si(OH)_{4\,(aq)} + Si(OH)_{4\,(aq)} \rightarrow (HO)_3Si–O–Si(OH)_{3\,(aq)} + H_2O_{\,(l)} \quad \text{(Reaction 2)}$$

Aging the hydrogel for 24 hours at room temperature allows further polycondensation and Ostwald ripening, which strengthens the wet silica network and reduces skeletal brittleness (Iswar *et al.*, 2017). However, drying this hydrogel under ambient pressure conditions typically induces severe capillary stress at the liquid-gas interface, leading to pore shrinkage and network collapse. To prevent this structural collapse, surface modification (silylation) was performed in a co-solvent system of TMCS, ethanol, and n-hexane (Halim *et al.*, 2024). The surface silylation of the wet gel is governed by a network of competing hydrolysis, esterification, and nucleophilic substitution reactions (Reactions 3 – 9).

$$2(CH_3)_3SiCl_{(l)} + H_2O(l) \rightarrow (CH_3)_3Si–O–Si(CH_3)_{3(l)} + 2HCl_{(aq)} \quad \text{(Reaction 3)}$$

$$(CH_3)_3SiCl_{(l)} + CH_3CH_2OH_{(l)} \rightarrow (CH_3)_3Si–O–CH_2CH_3(l) + HCl_{(aq)} \quad \text{(Reaction 4)}$$

$$2(CH_3)_3Si–O–CH_2CH_{3(l)} + H_2O_{(l)} \rightarrow (CH_3)_3Si–O–Si(CH_3)_{3(l)} + 2CH_3CH_2OH_{(l)} \quad \text{(Reaction 5)}$$

$$(CH_3)_3Si–O–Si(CH_3)_{3(l)} + 2HCl_{(aq)} \rightarrow 2(CH_3)_3SiCl_{(l)} + H_2O_{(l)} \quad \text{(Reaction 6)}$$

$$(CH_3)_3Si–O–CH_2CH_{3(l)} + HCl_{(aq)} \rightarrow (CH_3)_3SiCl_{(l)} + CH_3CH_2OH_{(l)} \quad \text{(Reaction 7)}$$

$$≡Si–OH + (CH_3)_3SiCl_{(l)} \rightarrow ≡Si–O–Si(CH_3)_3(s) + HCl_{(aq)} \quad \text{(Reaction 8)}$$

$$≡Si–OH + (CH_3)_3Si–O–CH_2CH_{3(l)} \rightarrow ≡Si–O–Si(CH_3)_{3(s)} + CH_3CH_2OH_{(l)} \quad \text{(Reaction 9)}$$

TMCS reacts rapidly with residual pore water within the hydrogel, producing highly reactive trimethylsilanol and HMDSO intermediates along with hydrochloric acid (Reactions 3 – 5). The introduction of ethanol as a co-solvent plays a vital role by esterifying TMCS to form ethoxytrimethylsilane (ETMS) (Reactions 6 – 7), which acts as a kinetic moderator, preventing rapid, localized silylation that would otherwise cause gel shattering. The

Copyright © 2026, Universitas Sebelas Maret, ISSN 1412-4092, e ISSN 2443-4183

primary silylating species, both TMCS and the intermediate ETMS, undergo nucleophilic attack by the surface silanol (≡Si–OH) groups of the silica gel. This chemical substitution anchors hydrophobic trimethylsilyl (–$Si(CH_3)_3$) groups directly onto the pore walls (Reactions 8 – 9), successfully transforming a highly polar, hydrophilic surface into a non-polar, low-surface-energy hydrophobic state (Mahadik *et al.*, 2016).

The hydrolysis and condensation kinetics are influenced by the pH of the sol, with an optimal gelation pH of 5.0. This value balances hydrolysis and condensation, minimizing gelation time to about 4 minutes and facilitating a uniform network. This strategy contrasts with that of Usgodaarachchi *et al.* (2021), who used surfactants at pH 4.0 to create mesoporous silica nanoparticles. This resin-free method aligns with the findings by Hardiane *et al.* (2023), which showed that cation exchange creates reactive silicic acid precursors that form stable gels. Thus, to dry the silica hydrogel without structural collapse, silylation is performed in a TMCS-ethanol/n-hexane system.

Effect of TMCS Content on Textural and Surface Characterization

The specific surface area, pore volume, porosity, density, and thermal conductivity of the dried aerogels were quantified across various silylation ratios, as shown in Table 1. The unmodified sample (1:0:1) had a specific surface area of 271 m^2/g and a pore volume of 0.34 cm^3/g, due to extensive collapse and shrinkage of the pore network caused by surface capillary stress during drying. As the ratio of TMCS silylation increased, the pore structure remained intact as capillary stress was minimized by replacing hydrophilic silanols with non-polar alkyl groups. At the ratio of 1:2:1 (optimized silylation ratio), the specific surface area increased to 795 m^2/g and pore volume increased to 5.75 cm^3/g, and porosity reached 97.8%. This represents an increase in pore volume compared to the mesoporous silica nanoparticles (MSN-A) reported by Usgodaarachchi *et al.* (2021), which exhibited a specific surface area of 150.28 m^2/g and a cumulative pore volume of 0.24 cm^3/g due to structural compaction during calcination. The cumulative pore volume also exceeds the values achieved by Feng *et al.* (2018), who reported a maximum surface area of 945.8 m^2/g and a pore volume of 0.889 cm^3/g using a 7/50 TMCS/n-hexane volume ratio.

Table 1. Structural and surface properties of ambient-pressure-dried rice husk silica aerogels.

Silica Aerogel Prepared	Surface area (m^2/g)	Pore volume (cm^3/g)	Porosity (%)	Water contact angle (°)	Thermal Conductivity (W/mK)
1:0:1	271	0.34	80.0	110	0.384
1:0.5:1	381	1.55	90.2	125	0.228
1:1:1	550	2.73	95.0	130	0.155
1:1.5:1	591	3.75	95.2	137	0.141
1:2:1	795	5.75	97.8	152	0.138

Superhydrophobicity (WCA > 150°) was achieved at a 1:2:1 ratio, with a water contact angle of 152°. This performance exceeds the contact angle of 138.5° obtained by Feng *et al.* (2018). The structural preservation achieved via this flexibility effect is further corroborated by Hardiane *et al.* (2023) who demonstrated that alkyl group substitution repels moisture and prevents adjacent pore walls from undergoing irreversible condensation during APD, leading to lower bulk densities. According to Hardiane *et al.* (2023), the modification of flexible polydimethylsiloxane (PDMS) yields the lowest density (0.4031 cm^3/g), while the aerogel examined in this research also features a similarly lightweight nanoporous structure with an extremely low thermal conductivity of 0.138 (W/m.K).The low surface energy reduced stress during solvent evaporation, allowing the pores to return to their original size after drying (Mahadik *et al.*, 2016). Thermal conductivity also decreased from 0.384 W/mK (1:0:1) to 0.138 W/mK (1:2:1), indicating a lightweight, insulating nanoporous aerogel structure.

Structural Characterization

FTIR Analysis

FTIR spectroscopy was employed to observe changes in functional groups and confirm the effectiveness of silylation at ambient temperature, covering a range from 400 to 4000 cm^{-1}. All spectra samples exhibited characteristics of the asymmetric stretching vibration of the Si–O–Si siloxane bond at 1054 – 1062 cm^{-1}, the symmetric Si–O–Si bending vibration near 792 cm^{-1}, and the O–Si–O bending vibration at 444 – 452 cm^{-1}, as summarized in Table 2. These peaks were also reported by Feng *et al.* (2018), Kaya and Deveci (2020), and Usgodaarachchi *et al.* (2021).

Copyright © 2026, Universitas Sebelas Maret, ISSN 1412-4092, e ISSN 2443-4183

For the modified aerogels (1:0.5:1 and 1:2:1), the silylation process was confirmed by the sharp Si–CH_3 stretching peak at 2950.99 cm^{-1} and the Si–O–CH_3 peak at 962.11 cm^{-1}, indicating the presence of nonpolar trimethylsilyl groups. Furthermore, the intensity of the broad O–H stretching band of hydrophilic silanol (≡Si–OH) groups (3000 – 3500 cm^{-1}) decreased in the modified aerogels. This matches the hydroxyl elimination mechanism analyzed by Goryunova *et al.* (2023). This hydrophobic surface modification is fundamentally different from the amine functionalization reported by Usgodaarachchi *et al*. (2021), which introduced polar, hydrophilic aminopropyl (APTES) groups marked by bending at 1557 cm^{-1} and CH_2 bending at 1479 cm^{-1} (Figure 4).

Table 2. Analysis of functional groups of rice husk silica aerogel.

Vibrational mode	FTIR peaks (cm^{-1})		
	RH unmodified	**RH modified 1:0,5:1**	**RH modified 1:2:1**
Si–O–Si *bending*	444.75	451.81	448.0
Si–O–Si *bending*	792.53	792.90	792.92
Si–O–CH_3 *stretching*	-	967.07	962.11
Si–O–Si *stretching*	1054.01	1061.95	1061.88
C–H *bending*	-	1559.97	1559.92
O–H *stretching*	1653.78	1629.59	1629.61
O–H *stretching*	2050	-	-
Si–CH_3 *stretching*	-	2950.96	2950.99
O–H *stretching*	3404.92	3397.51	3393.56

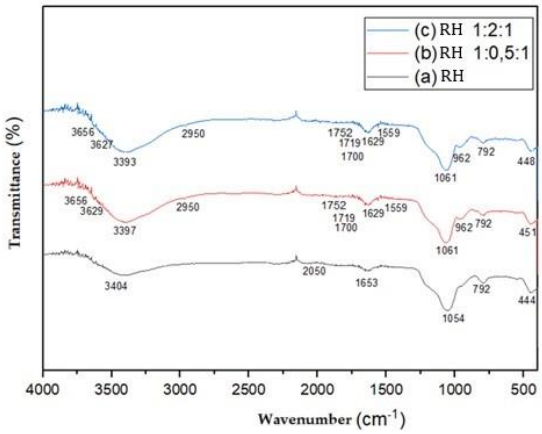


Figure 4. FTIR Spectrum of rice husk silica and modified rice husk in different ratios.

XRD Analysis

Figure 5 shows the X-ray diffraction patterns of rice husk ash and modified silica aerogel. The diffractogram showed a broad peak centered at 2θ = 22°. This broad peak indicates that the silica remains completely amorphous. This amorphous phase is in full agreement with the XRD findings of Zou and Yang (2019), Kaya and Deveci (2020), Ghani *et al.* (2022), indicating that calcination below 900 °C preserves the amorphous phase of RHA silica.

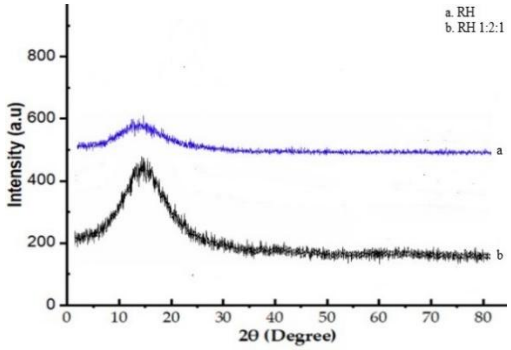


Figure 5. XRD Diffractogram of rice husk and rice husk modified 1:2:1.

Copyright © 2026, Universitas Sebelas Maret, ISSN 1412-4092, e ISSN 2443-4183

The modified aerogel (1:2:1) displays higher peak intensity compared to the raw ash; this difference does not suggest a transformation into a more organized structure, as the peak remains broad and non-crystalline (Reaction 8 – 9) (Stepien et al., 2019). Instead, the minor variation in intensity is likely due to differences in sample packing density, sample volume in the holder, or background scattering during the analysis. This confirms that surface silylation affects only the surface chemistry, without altering the amorphous silica backbone. The peaks in the modified silica gel were a result of the presence of Na^+ from the sodium hydroxide solution and Cl^- from the TMCS introduced during the surface modification process Khedkar *et al*. (2020).

Methylene Blue Adsorption

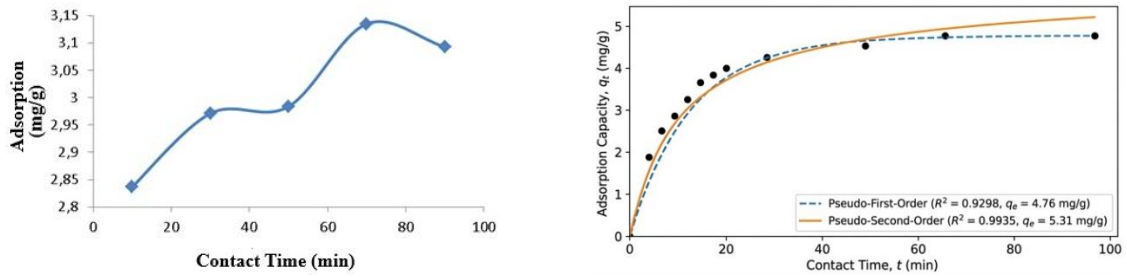
The hydrophobicity of TMCS-modified aerogel was confirmed through methylene blue adsorption. Methylene blue is measured at 665 nm using a UV-Vis spectrophotometer at room temperature, where it absorbs light most intensely (Munasir and Safitri, 2021). This wavelength offers high sensitivity, enabling the detection of low MB concentrations, which is essential for accurate adsorption analysis. Variations in contact time and initial concentration were evaluated to determine adsorption performance.

Adsorption Kinetics

The optimal contact time for Methylene Blue adsorption was examined using silica aerogels with various TMCS modification ratios. A 0.1 g sample of silica aerogel was contacted with 25 mL of 20 ppm methylene blue and shaken at 200 rpm for contact times of 10, 30, 50, 70, and 90 min. The mixtures were filtered through Whatman No. 42 filter paper, and the filtrate was analyzed with a UV-Vis spectrophotometer. Figure 6a shows that the silylated 1:2:1 aerogel achieved a maximum removal efficiency of 97.9% (qt = 3.1349 mg/g) at 70 minutes. In comparison, unmodified silica exhibited lower adsorption efficiency, with 64.9% removal (qt = 2.0774 mg/g). This improvement is attributed to the enhanced hydrophobicity and increased reactive sites from TMCS modification (Nazriati *et al*., 2019; Tanheitafino *et al*., 2020; Usgodaarachchi *et al*., 2021).

To investigate the mass transfer and chemisorption mechanisms, experimental data were analyzed using non-linear regression with Pseudo-First-Order (PFO) and Pseudo-Second-Order (PSO) models. Kinetic analysis of the data (Figure 6b) reveals rapid mass transfer within the adsorbent. Nonlinear modeling of kinetic data indicates that the PSO model (R^2= 0.9935) is better than the PFO model (R^2= 0.92980). The equilibrium adsorption capacity calculated using the PSO model (Q_e = 5.3116 mg/g) closely matches the experimental capacity (4.90 mg/g).

This adsorption process is driven by electrostatic interactions and hydrogen bonding between the cationic nitrogen center of the MB molecules and the electronegative oxygen atoms of the modified siloxane (≡Si–O-Si≡) network. Usgodaarachchi *et al.* (2021) also reported that MB adsorption onto RHA-derived silica follows the PSO kinetic model (R^2>0.99), their amine-functionalized silica (APTES) suffered a drastic drop in adsorption capacity. As explained by Usgodaarachchi *et al.* (2021), the protonation of grafted amine groups (NH_3^+) at pH < 9.8 generates a positive surface charge that electrostatically repels cationic MB molecules. TMCS-silylated aerogel replaces polar silanols without introducing repulsive positive charges, allowing the massive pore volume (5.75 cm^3) to adsorb MB without electrostatic barriers.



(a) (b)

Figure 6. Relationship between adsorption capacity and contact time (a) effect of contact time on methylene blue adsorption and (b) kinetic models.

Adsorption Isotherm

Variations in the initial concentration of methylene blue dye were tested to determine the maximum adsorption capacity of the silica aerogel and its effect on the adsorption efficiency. A 25 mL methylene blue solution was prepared at concentrations of 20, 30, 40, 50, and 60 ppm, with 0.1 g of 1:2:1 silica aerogel. The samples were shaken at 200 rpm for 70 min. The adsorption isotherms in this research illustrate the interaction

Copyright © 2026, Universitas Sebelas Maret, ISSN 1412-4092, e ISSN 2443-4183

between MB and the 1:2:1 aerogel. The effect of initial methylene blue concentration on adsorption capacity is presented in Figure 7a. The correlation between Q_e and C_e is typically represented by several isotherm models; for this analysis, the Langmuir and the Freundlich models were chosen. The corresponding Langmuir and the Freundlich isotherm plots are presented in Figures 7b and 7c, respectively. The Langmuir adsorption isotherm was initially created as an empirical model that assumes monolayer adsorption on a surface with a fixed, limited number of localized sites. This model presumes uniform adsorption energy across the surface, with no lateral interactions or steric hindrance between adjacent adsorbed molecules (Usgodaarachchi *et al.*, 2021). The linear form of the Langmuir equation is expressed as follows (Equations 3 and 4).

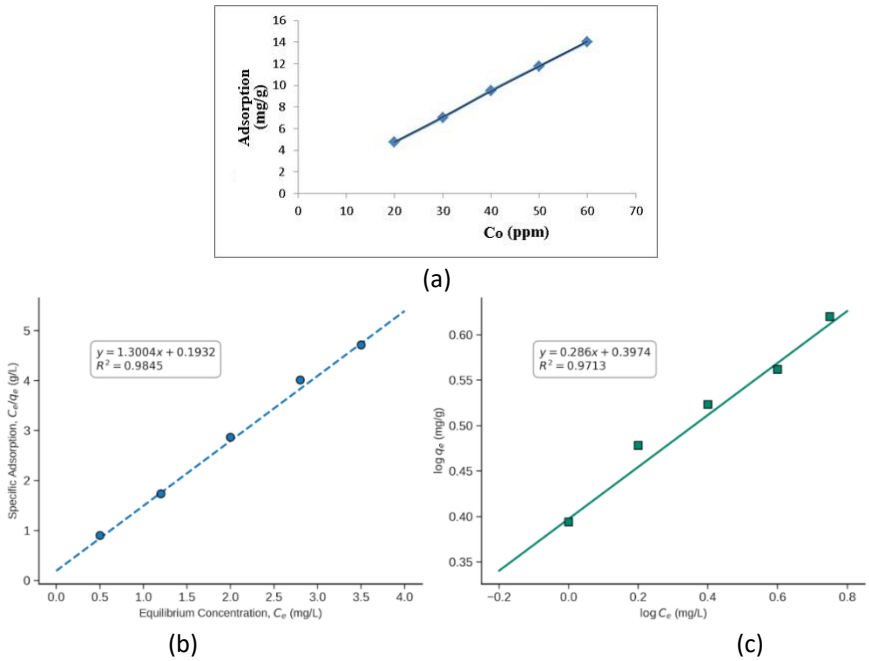


Figure 7. Effect of initial methylene blue concentration on adsorption isotherm: (a) adsorption capacity as a function of initial methylene blue concentration, (b) Langmuir isotherm plot, and (c) Freundlich isotherm plot.

Based on Figures 7b and 7c, the Langmuir model yielded a higher coefficient of determination ($R^2 = 0.9845$) compared to the Freundlich model ($R^2 = 0.9713$). The Langmuir model confirms that the adsorption of MB onto silylated silica aerogels occurs as a monolayer on a homogeneous adsorbent surface with energetically equivalent active sites. Once an active site is occupied by a cationic MB molecule, no further adsorption can occur at that specific site, indicating a uniform, localized chemical binding interface (Wang and Guo, 2020). This high performance is further supported by Goryunova *et al.* (2023), who reviewed how tailoring the physical properties of silica aerogels leads to excellent dye adsorption capacities, making them competitive, eco-friendly, and cost-effective alternatives for wastewater treatment.

CONCLUSION

This study presents the synthesis of superhydrophobic silica aerogels from rice husk ash (RHA) using a cost-effective ambient pressure drying method. Chemical silylation with a TMCS/ethanol/n-hexane co-solvent prevented network collapse. The optimal 1:2:1 ratio yielded a specific surface area of 795 m^2/g, pore volume of 5.75 cm^3/g, and porosity of 97.8%, with a low thermal conductivity of 0.138 W/(m·K). FTIR spectroscopy confirmed the attachment of trimethylsilyl groups, resulting in a Water Contact Angle of 152°. Adsorption tests showed a 97.9% Methylene Blue removal efficiency within 70 minutes, consistent with the Pseudo-Second-Order and Langmuir models. These results highlight the potential of silylated silica aerogels from rice husk as effective, low-cost adsorbents for wastewater treatment.

CONFLICT OF INTEREST

There is no conflict of interest in this article

Copyright © 2026, Universitas Sebelas Maret, ISSN 1412-4092, e ISSN 2443-4183

AUTHOR CONTRIBUTION

DS: Conceptualization, Methodological Designs, Supervision, and Project Administration; EE: Data Analysis, Experiment, Review, and Editing Manuscript; DKN: Investigation, Managing and Curating the Data, Preparing the Initial Manuscript Draft, and Creating the Visualizations. All authors have read and approved the final version of the manuscript.

ACKNOWLEDGEMENT

We acknowledge the financial support from the LPPM Universitas Bojonegoro for research materials through Project Number 084/LPPM-LIT/UB/V/2025, as well as publication assistance from Kemendiktisaintek under contract number 0488/C/DT.06.01/2005.

DECLARATION OF GENERATIVE AI

During the preparation of this work, the authors used Grammarly in order to improve readability and paraphrase text. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

REFERENCES

Andini, A.M., Azmiyawati, C., and Darmawan, A., 2022. Effect of pH on the Synthesis of Silica Sol-Gel Tetraethylorthosilicate-Trimethylchlorosilan (TEOS-TMCS). *Jurnal Kimia Sains dan Aplikasi*, 25, 394–398. https://doi.org/10.14710/jksa.25.11.394-398.

Bangi, U.K.H., Ransing, A.A., Dhavale, R.P., Park, H.-H., and Patil, V.B., 2024. Improvement in the Characteristics of Ambient Pressure Dried Silica Aerogels for Thermal Insulation Purpose. *Journal of Porous Materials*, 31, 115–123. https://doi.org/10.1007/s10934-023-01500-9.

Feng, Q., Chen, K., Ma, D., Lin, H., Liu, Z., Qin, S., and Luo, Y., 2018. Synthesis of High Specific Surface Area Silica Aerogel from Rice Husk Ash Via Ambient Pressure Drying. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 539, 399–406. https://doi.org/10.1016/j.colsurfa.2017.12.025.

Ghani, U., Hussain, S., Ali, A., Tirth, V., Algahtani, A., Zaman, A., Mushtaq, M., Althubeiti, K., and Aljohani, M., 2022. Hydrothermal Extraction of Amorphous Silica from Locally Available Slate. *ACS Omega*, 7, 6113–6120. https://doi.org/10.1021/acsomega.1c06553.

Goryunova, K., Gahramanli, Y., and Gurbanova, R., 2023. Adsorption Properties of Silica Aerogel-Based Materials. *RSC Advances*, 13, 18207–18216. https://doi.org/10.1039/D3RA02462H.

Halim, Z.A.A., Awang, N., Ahmad, N., and Yajid, M.A.M., 2024. Effects of Silane Concentration on Hydrophobic Conversion of Rice Husk-Derived Silica Aerogels Prepared by Supercritical Drying. *Biomass Conversion and Biorefinery*, 14, 15811–15821. https://doi.org/10.1007/s13399-022-03710-8.

Halim, Z.A.A., Yajid, M.a.M., and Hamdan, H., 2016. Synthesis and Characterization of Rice Husk Ash Derived - Silica Aerogel Beads Prepared by Ambient Pressure Drying. *Key Engineering Materials*, 694, 106–110. https://doi.org/10.4028/www.scientific.net/KEM.694.106.

Hardiane, E.R., Purba, G.E.M., and Dahliyanti, A., 2023. Transparency and Thermal Stability of Silica Aerogel Synthesized from Sodium Silicate Using Ambient Pressure Drying. *Journal of Emerging Supply Chain, Clean Energy, and Process Engineering*, 2, 125–130. https://doi.org/10.57102/jescee.v2i2.68.

Hidayatulloh, C.Y., Iskandar, A.S., Al-ayubi, S., Permanasari, A. R., dan Kunci, K., 2021. Kajian Pustaka Pemanfaatan Silika Sekam Padi sebagai Aerogel Adsorben untuk Menurunkan Kandungan Logam pada Air. *Prosiding the 12th Industrial Research Workshop and National Seminar*, 4–5 Agustus 2021, Bandung 779–784.

Iswar, S., Malfait, W.J., Balog, S., Winnefeld, F., Lattuada, M., and Koebel, M.M., 2017. Effect of Aging on Silica Aerogel Properties. *Microporous and Mesoporous Materials*, 241, 293–302. https://doi.org/10.1016/j.micromeso.2016.11.037.

Karamikamkar, S., Naguib, H.E., and Park, C.B., 2020. Advances in Precursor System for Silica-Based Aerogel Production Toward Improved Mechanical Properties, Customized Morphology, and Multifunctionality: A Review. *Advances in Colloid and Interface Science*, 276, 102101. https://doi.org/10.1016/j.cis.2020.102101.

Kaya, G.G., and Deveci, H., 2020. Synergistic Effects of Silica Aerogels/Xerogels on Properties of Polymer Composites: A Review. *Journal of Industrial and Engineering Chemistry*, 89, 13–27. https://doi.org/10.1016/j.jiec.2020.05.019.

Copyright © 2026, Universitas Sebelas Maret, ISSN 1412-4092, e ISSN 2443-4183

Khedkar, M.V., Jadhav, S.A., Somvanshi, S.B., Kharat, P.B., and Jadhav, K.M., 2020. Physicochemical Properties of Ambient Pressure Dried Surface Modified Silica Aerogels: Effect of pH Variation. *SN Applied Sciences*, 2, 696. https://doi.org/10.1007/s42452-020-2463-3.

Len, A., Paladini, G., Románszki, L., Putz, A.-M., Almásy, L., László, K., Bálint, S., Krajnc, A., Kriechbaum, M., Kuncser, A., Kalmár, J., and Dudás, Z., 2021. Physicochemical Characterization and Drug Release Properties of Methyl-Substituted Silica Xerogels Made Using Sol–Gel Process. *International Journal of Molecular Sciences*, 22, 9197. https://doi.org/10.3390/ijms22179197.

Li, P., Yang, C., Xu, X., Miao, C., He, T., Jiang, B., and Wu, W., 2022. Preparation of Bio-Based Aerogel and Its Adsorption Properties for Organic Dyes. *Gels* 8, 755. https://doi.org/10.3390/gels8110755.

Liu, H., Liu, J.A., Tian, Y., Jiao, J., and Wu, X., 2022. Thermal Insulation Performance of Silica Aerogel Composites Doped with Hollow Opacifiers: Theoretical Approach. *Gels*, 8, 295. https://doi.org/10.3390/gels8050295.

Mahadik, S.A., Pedraza, F., Parale, V.G., and Park, H.-H., 2016. Organically Modified Silica Aerogel with Different Functional Silylating Agents and Effect on Their Physico-Chemical Properties. *Journal of Non-Crystalline Solids*, 453, 164–171. https://doi.org/10.1016/j.jnoncrysol.2016.08.035.

Mahardhika, M.K., and Muldarisnur, M., 2021. Sintesis dan Karakterisasi Silika Aerogel sebagai Adsorben Tumpahan Minyak. *Jurnal Fisika Unand*, 10, 296–302. https://doi.org/10.25077/jfu.10.3.296-302.2021.

Munasir, M. and Safitri, I.I., 2021. Hydrophobic Nanoparticles-Silica from Natural Sands with TMCS as Media. *IOP Conference Series: Materials Science and Engineering*, 1125, 012005. https://doi.org/10.1088/1757-899X/1125/1/012005.

Nazriati, N., Maknun, L., and Fajaroh, F., 2019. Removal Methylene Blue from Aqueous Solution Using Silica Aerogel Prepared from Bagasse Ash. *IOP Conference Series: Earth and Environmental Science*, 299, 1–6. https://doi.org/10.1088/1755-1315/299/1/012044.

Pisal, A.A., and Rao, A.V., 2016. Comparative Studies on the Physical Properties of TEOS, TMOS and Na_2SiO_3 Based Silica Aerogels by Ambient Pressure Drying Method. *Journal of Porous Materials*, 23, 1547–1556. https://doi.org/10.1007/s10934-016-0215-y.

Ren, L., Sun, S., Dong, Q., and Wang, H., 2022. Study on Silica Aerogel Modified by Trimethylchlorosilane. *Journal of Physics: Conference Series* 2393, 012026. https://doi.org/10.1088/1742-6596/2393/1/012026.

Stepien, A., Leśniak, M., and Sitarz, M., 2019. A Sustainable Autoclaved Material Made of Glass Sand. *Buildings* 9, 232. https://doi.org/10.3390/buildings9110232.

Tanheitafino, S., Shofiyani, A., Sasri, R., and Rudiyanshah, R., 2020. Synthesis and Characterization of Trimethylchlorosilane Modified Silica Xerogel. *Jurnal Kimia Sains dan Aplikasi*, 23, 249–254. https://doi.org/doi.org/10.14710/jksa.23.7.249-254.

Usgodaarachchi, L., Thambiliyagodage, C., Wijesekera, R., and Bakker, M.G., 2021. Synthesis of Mesoporous Silica Nanoparticles Derived from Rice Husk and Surface-Controlled Amine Functionalization for Efficient Adsorption of Methylene Blue from Aqueous Solution. *Current Research in Green and Sustainable Chemistry*, 4, 100116. https://doi.org/10.1016/j.crgsc.2021.100116.

Wang, J., and Guo, X., 2020. Adsorption Isotherm Models: Classification, Physical Meaning, Application and Solving Method. *Chemosphere*, 258, 127279. https://doi.org/10.1016/j.chemosphere.2020.127279.

Zou, Y., and Yang, T., 2019. Rice Husk, Rice Husk Ash and Their Applications. *Rice Bran and Rice Bran Oil*, Elsevier, 207–246. https://doi.org/10.1016/B978-0-12-812828-2.00009-3.

(cc) BY-NC Copyright © 2026, Universitas Sebelas Maret, ISSN 1412-4092, e ISSN 2443-4183