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Synthesis of Hydrophobic Silica Xerogel from Fly Ash for Oil–in–Water Adsorption

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Abstract

In this study, silica xerogel was synthesized from coal fly ash modified with trimethylchlorosilane (TMCS) reagent to increase the hydrophobicity of the material. TMCS-modified silica xerogel was then used for oil adsorption in water. Silica xerogel was synthesized using the sol-gel method with sodium silicate from fly ash as a precursor and citric acid as a catalyst. The sol-gel process involves sequential steps of hydrolysis and condensation, followed by gelation (the sol-to-gel transition) and aging. Surface modification of the resulting silica xerogel was conducted using TMCS in a mixture of methanol and petroleum benzine, with volume ratios of TMCS:methanol:petroleum benzine set at 0:1:1, 1:1:1, 2:1:1, and 3:1:1. The synthesized silica xerogel was characterized using FTIR spectroscopy, SEM, GSA, and contact angle measurements to evaluate its hydrophobicity. FTIR spectrophotometry results revealed that silica modified with TMCS exhibited absorption bands corresponding to Si–CH$_3$ groups at 843.20, 845.69, and 843.18 cm^{-1}. These findings indicate the successful formation of silyl groups on the surface of the silica xerogel when using TMCS:methanol:phosphate buffer ratios of 0:1:1, 1:1:1, 2:1:1, and 3:1:1. SEM analysis revealed that the surface morphology of the synthesized silica xerogel exhibited a porous structure with a mesoporous pore size distribution. Based on the experimental results, it can be concluded that surface modification with TMCS enhances the hydrophobicity of the silica xerogel. An increase in TMCS volume led to a corresponding increase in hydrophobicity. The hydrophobic silica xerogel demonstrated a good adsorption capacity for oil in water, ranging from 6 to 22 mg/g, with the adsorption capacity increasing in accordance with the degree of hydrophobicity.

1. Introduction

Silica is a widely used chemical material with applications across various fields. It is formed through the polymerization of silicic acid and consists of tetrahedral SiO$_4$ units, with the general formula SiO$_2$. Naturally occurring silica typically has a crystalline structure, while its synthetic form is generally amorphous [1]. Besides being found in natural mineral deposits, silica can also be synthesized from silica-rich waste materials, such as coal fly ash [2].

Although rice husk ash has been commonly utilized as a silica source, this approach is already well established. In this study, coal fly ash was selected as an alternative silica source due to its abundance in the Kalimantan region, which hosts at least 14 coal-fired power plants operated by PLN and private companies. The widespread development of these power plants has led to the significant production of fly ash as a by-product [3]. PT. Indonesia Chemical Alumina (ICA), located in West Kalimantan, is one such facility, producing fly ash with a silica content of 48.05% [4].

The main components of coal fly ash are silica (SiO$_2$), alumina (Al$_2$O$_3$), and iron oxide (Fe$_2$O$_3$), along with smaller amounts of carbon, calcium, magnesium, and sulfur [5]. Given its relatively high silica content, fly ash is a promising raw material for silica extraction, which can enhance its value as an adsorbent. Previous studies have shown that silica has good adsorption performance for organic pollutants, including oil-based waste [6].

The widespread use and high export volume of palm oil, along with the expansion of plantation areas, have led to a significant increase in palm oil mill waste [7]. This waste, particularly liquid effluent, contains high levels of pollutants and poses a serious threat to aquatic environments [8]. To address this issue, oil adsorption from water using silica-based adsorbents offers a promising solution. The process is relatively simple, cost-effective, and has the potential to reduce environmental pollution. Hydrophobic silica xerogel, in particular, improves affinity for oil, supporting both water purification and potential oil recovery.

Silica is an inert, hydrophilic material with high thermal and mechanical stability and low solubility in organic solvents [1]. In contrast, oil is a hydrophobic organic compound. The adsorption capacity of silica for oil can be significantly improved by modifying its surface to become hydrophobic. This is achieved by converting hydrophilic silanol groups (Si–OH) into hydrophobic trimethylsilyl groups ($Si–(CH_3)_3$) through a silylation reaction using trimethylchlorosilane (TMCS) [9].

Several studies have demonstrated the effectiveness of hydrophobic silica in adsorbing hydrophobic organic compounds. For instance, Bramantya *et al.* [10] reported that TEOS-derived hydrophobic silica aerogel had an oil adsorption capacity of 13.98 g/g. Oktavian *et al.* [11] showed that hydrophobic silica membranes improved crude biodiesel purity during purification processes.

Silica exists in various physical forms, including hydrogel, xerogel, and aerogel. Among these, xerogel is widely used as an adsorbent due to its large surface area, high pore volume, and robust mechanical properties [12]. To improve its performance in adsorbing organic pollutants like oil, surface modification is necessary to render the xerogel hydrophobic, typically through silylation using TMCS.

The degree of hydrophobicity achieved depends on the extent of silanol-to-silyl group conversion, which is influenced by the silica's polymerization level, solvent type, and TMCS concentration. Silylation is typically conducted in non-polar solvents such as n-hexane [13]. However, Tanheitafino *et al.* [14] reported a successful synthesis of highly hydrophobic silica using petroleum benzine, another non-polar solvent, as evidenced by high contact angle values.

Petroleum benzine is favored due to its excellent solubility for TMCS, inertness, low toxicity compared to n-hexane, and low boiling point (40–60°C), which allows easy removal by evaporation. In this study, a co-solvent system of petroleum benzine and methanol was used. Methanol was chosen for its amphiphilic nature, acting as a phase mediator to facilitate the silylation process. TMCS was selected for surface modification due to its high reactivity compared to other organosilanes [15].

Previous research by Tanheitafino *et al.* [14] focused mainly on synthesizing and characterizing hydrophobic silica xerogel, without exploring its application in adsorption processes. Applications in biodiesel purification [11] and metal removal using silica aerogel from rice husk ash. Hidayatulloh *et al.* [16] demonstrate its versatility, but the synthesis of hydrophobic silica xerogel from fly ash using TMCS in petroleum benzine has not yet been reported.

Therefore, this study investigates the synthesis of hydrophobic silica xerogel using sodium silicate derived from coal fly ash. The effect of TMCS concentration in petroleum benzine–methanol solvents on the resulting material's hydrophobicity is explored. The synthesized material is then applied to oil adsorption in water, with adsorption capacity evaluated using the Langmuir and the Freundlich isotherm models.

Characterization of the materials was conducted using X-ray fluorescence (XRF), X-ray diffraction (XRD), and Fourier-transform infrared spectroscopy (FTIR). Hydrophobicity was assessed via contact angle measurements, while adsorption performance was analyzed based on the capacity of the xerogel to adsorb oil from water.

2. Experimental

2.1. Tools and Materials

The equipment used in this study included a US analytical balance (maximum capacity: 150 g), magnetic stirrer, Arzeeth Laboratory Equipment LD-15L-EI oven, Labec Laboratory furnace, water bath, a complete set of glassware, PANalytical Epsilon 3 XRF analyzer, Bruker D2 Phaser XRD, Nicolet Avatar 360 IR FTIR spectrophotometer, Quantachrome Novatouch LX4 surface area analyzer, and a contact angle measurement setup. The contact angle setup consisted of a high-resolution camera (Canon 1200D), a magnifying glass, a 26G syringe, and specially prepared xerogel and aerogel plates. These components were assembled on a stand, as shown in Figure 1.

The sample used in this study was fly ash obtained from the waste of PT. Indonesia Chemical Alumina (ICA), located in Tayan, Sanggau Regency, West Kalimantan. The chemicals used included methanol (CH_3OH), citric acid monohydrate ($C_6H_8O_7.H_2O$), petroleum benzine, trimethylchlorosilane (TMCS), sodium hydroxide (NaOH), and hydrochloric acid (HCl). All chemicals were of pro-analysis grade.

Figure 1. Contact angle measurement setup

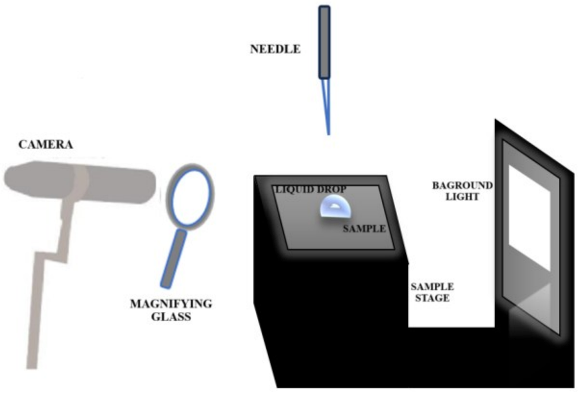


Figure 2. Two-dimensional design of the contact angle measurement setup

2.2. Sample Preparation

A total of 250 g of fly ash was washed with warm water to remove water-soluble organic and inorganic impurities that could interfere with the silica extraction process. The washed samples were then dried at 105°C for 3 hours. After drying, the samples were sieved using a 100-mesh sieve and soaked in 1 M HCl at a 1:2 (w/v) ratio. The mixture was stirred using a magnetic stirrer at 150 rpm for 30 minutes. The samples were then rinsed with distilled water until a neutral pH was reached and dried again at 105°C for 3 hours. The dried samples were once more sieved using a 100-mesh sieve. Finally, the pretreated fly ash was analyzed using XRF, XRD, and FTIR spectrophotometry.

2.3. Silica Extraction from Fly Ash Samples

A total of 125 g of fly ash and 25 g of solid NaOH were placed into a porcelain crucible and calcined at 500°C for approximately 5 hours. The resulting calcined material was then mixed with distilled water until the yellow color of the extract faded. The mixture was filtered to separate the filtrate. To precipitate silica, 2 M HCl was gradually added to the filtrate until the pH reached 8–9, resulting in gel formation. The gel was then left to age for 2 hours. The precipitated silica was washed repeatedly with distilled water until a neutral pH was achieved, followed by drying in an oven at 105°C for approximately 5 hours. The isolated silica was characterized using XRF, XRD, and FTIR spectrophotometry. Subsequently, 10 g of the dried silica was ground and dissolved in 4 M NaOH to obtain the sodium silicate precursor.

2.4. Synthesis of TMCS-modified Silica Xerogel

Silica xerogel was synthesized using the sol-gel method, following the procedure by Tanheitafino *et al.* [14], with sodium silicate precursor extracted from fly ash. The sodium silicate solution, initially at a specific gravity of 1.3057 g/mL, was diluted to 1.05 g/mL. The sol was prepared by mixing 20 mL of this diluted sodium silicate with 2 mL of 2 M citric acid under continuous stirring, during which gelation occurred. The resulting hydrogel was aged at 50°C for 3 hours to strengthen its structure. After aging, the hydrogel was washed with distilled water until a neutral pH was achieved, then filtered to separate it from the wash water. Subsequently, the water in the hydrogel was replaced by soaking it in methanol for 24 hours. After this soaking period, the alcogel was separated from the solvent by filtration.

Surface modification of the synthesized silica xerogel was performed using TMCS reagent in a solvent mixture of methanol and petroleum benzine. The volume ratios of TMCS:methanol:petroleum benzine varied as 0:1:1, 1:1:1, 2:1:1, and 3:1:1. The reaction proceeded for 24 hours, after which the modified gel was separated from the solvent by filtration. The filtered gel was initially dried at room temperature for 24 hours, followed by drying at 50°C until a constant weight was achieved.

2.5. Characterization of Silica Xerogel

Characterization of the TMCS-modified silica xerogel was conducted using FTIR spectrophotometry, SEM-EDX, and SAA. The hydrophobic properties were evaluated by measuring the contact angle (θ) of a drop of distilled water on the silica surface. A small drop of distilled water was carefully placed onto the silica surface using a fine hypodermic needle, and a photograph was taken immediately after contact. The contact angle was defined as the angle formed between the water droplet and the silica surface. A highly hydrophilic surface exhibits a contact angle close to 0°, a hydrophobic surface shows a contact angle greater than 90°, and a superhydrophobic surface has a contact angle exceeding 150° [17].

2.6. Adsorption Ability Test of Hydrophobic Silica Xerogel for Oil in Water

Palm oil samples weighing 0, 0.02, 0.04, 0.08, and 0.1 g were each mixed with 50 mL of water in separate bottles. The mixtures were shaken at 100 rpm for 15 minutes. Subsequently, 0.025 g of unmodified silica xerogel (TMCS ratio 0:1:1) and TMCS-modified silica xerogels with volume ratios of 1:1:1, 2:1:1, and 3:1:1 were each added to 50 mL of water in separate bottles. These mixtures were shaken at 120 rpm for 1 hour. After adsorption, the adsorbent was carefully separated using Whatman filter paper No. 42 until dripping ceased. The filter paper with the adsorbent was weighed, then dried in an oven at 100°C until constant weight was achieved. The dried filter paper and adsorbent were weighed again. A control experiment without adsorbent was conducted under the same conditions. The adsorption capacity of the hydrophobic silica xerogel for oil in water was determined using the Langmuir and the Freundlich isotherm models.

3. Results and Discussion

3.1. XRF Analysis of Coal Fly Ash and Synthesized Silica

Coal fly ash and the synthesized silica samples were characterized before the extraction process using XRF, XRD, and FTIR spectroscopy. Although this study did not determine the yield, Pratiwi *et al.* [18] reported a silica yield of 36.02% from fly ash.

3.1.1. XRF Analysis of Coal Fly Ash and Synthesized Silica

XRF analysis was performed to determine the elemental and oxide composition of the coal fly ash and synthesized silica samples. The results are presented in

Tables 1 and 2. The XRF results presented in Table 1 indicate that the fly ash sample primarily consists of silica and alumina, which is consistent with the XRD data shown in Figure 3. The silica content (SiO_2) is approximately 67%, followed by alumina at 17%, with other oxides present in smaller amounts. Based on the XRF and XRD analyses, the fly ash sample can be classified as Class F fly ash, which is derived from coal combustion residue and characterized by a CaO content below 10% and pozzolanic properties, according to ASTM Standard C618. Table 2 shows that silica was successfully synthesized with a purity of 95%. The high concentration of SiO_2 confirms the suitability of the extracted silica for further synthesis into silica xerogel.

3.1.2. XRD Analysis of Coal Fly Ash and Synthesized Silica

Based on the XRD results processed with Match! version 3 software, shown in Figure 3, the fly ash sample contains primarily silica minerals in the form of quartz and cristobalite, as well as alumina minerals such as corundum and mullite. Figure 4 displays the XRD pattern of the synthesized silica, which exhibits an amorphous structure characterized by a broad peak at 2θ = 23.25°. According to the Joint Committee on Powder Diffraction Standards (JCPDS), as referenced in Putrinesia *et al.* [19], the SiO_2 peak typically appears within the 2θ range of 20.85° to 26.65°. The amorphous nature of the silica gel is beneficial for further modification processes, as it tends to be more reactive compared to crystalline forms.

Table 1. XRF analysis results of coal fly ash composition

Element	% Relative weight	Oxide compound	% Relative weight
Si	59.422	SiO_2	66.919
Al	15.447	Al_2O_3	17.62
P	2.872	P_2O_5	3
Ca	2.577	CaO	1.521
Ti	2.529	TiO_2	1.72
Fe	15.11	Fe_2O_3	8.197

Table 2. Results of XRF analysis on extracted silica

Element	% Relative weight	Oxide compounds	% Relative weight
Si	95.05	SiO_2	95.57
Al	2.464	Al_2O_3	2.995
P	1.099	P_2O_5	0.839
Ca	0.531	CaO	0.24
Ti	0.044	TiO_2	0.023
Fe	0.344	Fe_2O_3	0.154

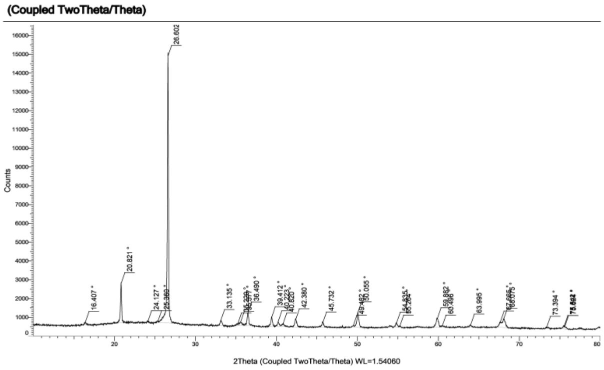


Figure 3. XRD pattern of coal fly ash

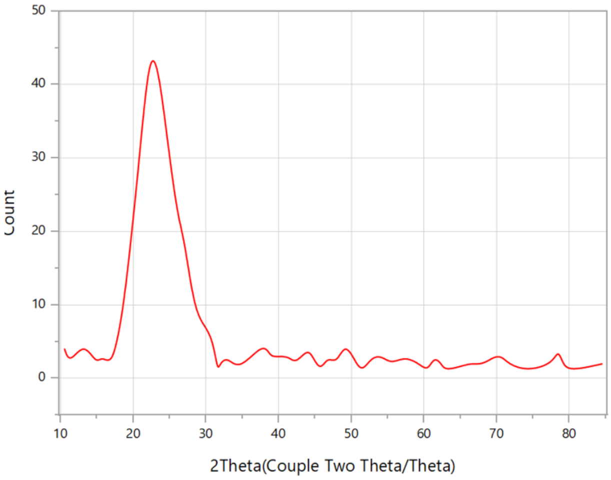


Figure 4. XRD analysis result of synthesized silica

3.1.3. FTIR Analysis of Coal Fly Ash and Synthesized Silica

To identify the functional groups present in coal fly ash and the synthesized silica, FTIR spectroscopy was performed. The results of this characterization are presented in Figure 5.

Based on the spectral data in Figure 5, the fly ash spectrum shows an absorption band at 3444.87 cm^{-1}, corresponding to the stretching vibration of the –OH group. A broad and sharp band at 1099.43 cm^{-1} indicates the asymmetric stretching vibration of Si–O–Si, reflecting the presence of Si–O or Al–O groups. The absorption at 798.53 cm^{-1} corresponds to the symmetric stretching vibration of Si–O–Si, followed by a bending mode of Si–O at 468.70 cm^{-1}. These FTIR results support the XRD and XRF data, confirming that fly ash primarily consists of silica and alumina compounds, with minor impurities such as iron oxide and other minerals.

The FTIR spectrum of synthesized silica, also shown in Figure 5, exhibits characteristic functional groups: Si–O–Si bending vibration at 466.77 cm^{-1}, symmetric stretching at 800.46 cm^{-1}, and asymmetric stretching at 1093.64 cm^{-1}, all indicative of a Si–O–Si (siloxane) framework. Additionally, a peak at 3450.65 cm^{-1} corresponds to –OH stretching vibrations, while a peak at 1641.42 cm^{-1} indicates bending vibrations of Si–OH (silanol groups), confirming the presence of silanol on the silica surface.

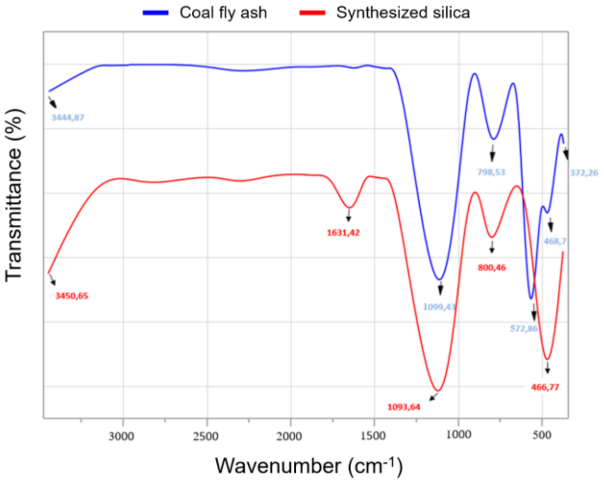


Figure 5. FTIR spectra of coal fly ash and synthesized silica

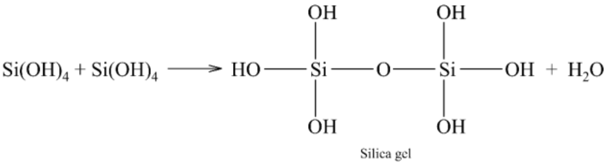
3.2. Characteristics of Unmodified Silica Xerogel and TMCS-Modified Silica

The synthesis of TMCS-modified silica xerogel was carried out using the sol-gel method, following the procedure described by Tanheitafino *et al.* [14], with sodium silicate precursor derived from silica. This process involves the formation of a sol and its transition to a gel through hydrolysis and condensation of precursor molecules, followed by gelation, aging, and drying stages.

The next stage involves the gradual condensation of the sol to form a gel, creating an interconnected polymer-like network. The silica polymers, containing water molecules, form a hydrogel structure that is aged (ripened) for 3 hours at 50°C to strengthen the network. Following this, the silica surface was modified to replace the hydrophilic Si–OH groups with hydrophobic Si–O–Si(CH_3) groups. This modification was performed using TMCS reagent in a solvent mixture of methanol and petroleum benzine, with TMCS volume ratios varied at 0:1:1, 1:1:1, 2:1:1, and 3:1:1. The modified silica xerogel was dried at 50°C to remove any remaining solvents attached to the gel. Subsequently, characterization was performed using FTIR spectroscopy, SEM-EDX, and SAA.

$$\underset{\text{Sodium silicate}}{Na_2SiO_3} + H_2O + \underset{\substack{\text{Citric acid}\\\text{monohydrate}}}{2C_6H_8O_7.H_2O} \rightarrow \underset{\text{Orthosilicic acid}}{Si(OH)_4} + \underset{\substack{\text{Monosodium}\\\text{citrate}}}{2C_6H_8O_7Na} + 2H_2O$$

Figure 6. Hydrolysis of sodium silicate by water with citric acid catalyst



$$Si(OH)_4 + Si(OH)_4 \longrightarrow \underset{\text{Silica gel}}{HO-\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{Si}}-O-\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{Si}}-OH} + H_2O$$

Figure 7. Sol-to-gel condensation process

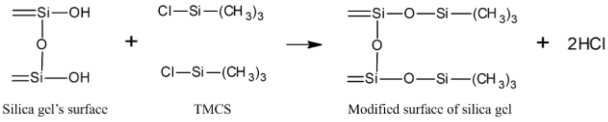


Figure 8. Silylation reaction on the surface of silica xerogel using TMCS

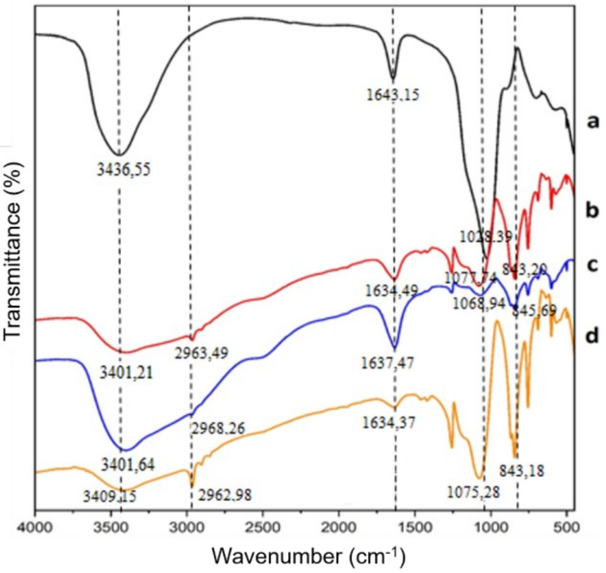


Figure 9. FTIR spectra of silica xerogel with varying TMCS:methanol:petroleum benzine volume ratios: (a) 0:1:1 (unmodified), (b) 1:1:1, (c) 2:1:1, and (d) 3:1:1

3.2.1. FTIR Analysis of Unmodified Silica Xerogel and TMCS-Modified Silica

FTIR analysis was conducted to identify changes in the functional groups of silica resulting from surface modification using TMCS reagent at various composition ratios. Figure 9 demonstrates the success of the surface modification process. The presence of Si–CH_3 groups is indicated by absorption peaks at wavenumbers 843.20, 845.69, and 843.18 cm^{-1} in Figures 9b, 9c, and 9d, respectively. Additionally, C–H stretching vibrations appear at 2963.49, 2968.26, and 2962.98 cm^{-1} in the same figures, confirming the partial replacement of silanol (Si–OH) groups with methyl groups. This modification is further supported by the decrease in intensity of the –OH stretching band around 3400 cm^{-1}, with the largest reduction observed in Figure 9d. These results indicate that higher TMCS concentrations lead to a greater substitution of silanol groups by trimethylsilyl groups (Si–$(CH_3)_3$).

3.2.2. SEM Analysis of Unmodified Silica Xerogel and TMCS-modified Silica

SEM characterization was performed to confirm the formation of a three-dimensional silica network, resulting in a porous xerogel structure, as shown in Figure 10. The images reveal an uneven surface with a wide range of grain sizes and irregular distribution across the silica xerogel surface. The SEM micrograph of unmodified silica xerogel (Figure 10a) shows significant particle agglomeration, forming large lumps. In contrast, the TMCS-modified silica samples (Figures 10b, 10c, and 10d) exhibit noticeably reduced agglomeration, especially at TMCS ratios of 2:1:1 (Figure 10c) and 3:1:1 (Figure 10d). This suggests that increasing the TMCS concentration decreases particle agglomeration, potentially increasing the silica surface area.

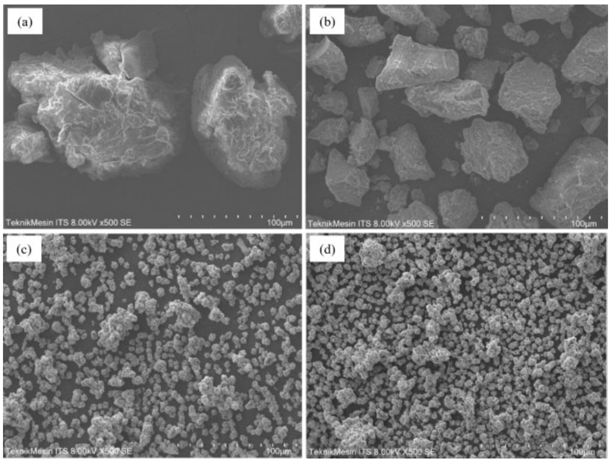


Figure 10. SEM images of silica xerogel at 500× magnification at different volume ratios of (a) 0:1:1, (b) 1:1:1, (c) 2:1:1, and (d) 3:1:1

3.2.3. EDX Analysis of Unmodified Silica Xerogel and TMCS-modified Silica

In addition to SEM, EDX analysis was conducted to determine the elemental composition of the samples, as shown in Figure 11. The EDX spectra reveal that the primary elements present are silicon (Si) and oxygen (O), confirming the silica composition. The detection of carbon (C) further indicates the successful incorporation of trimethylsilyl groups on the surface of the TMCS-modified silica xerogel.

3.2.4. SSA Analysis of Unmodified Silica Xerogel and TMCS-modified Silica

The SEM-EDX findings were further supported by SAA using the GSA method to determine the surface area, pore volume, and pore diameter of the synthesized xerogels, as summarized in Table 4. The results indicate that both unmodified and TMCS-modified silica xerogels have pore diameters ranging from 3.0 to 7.5 nm. According to IUPAC classification, these pore sizes categorize the xerogels as mesoporous materials (pore diameter between 2 and 50 nm).

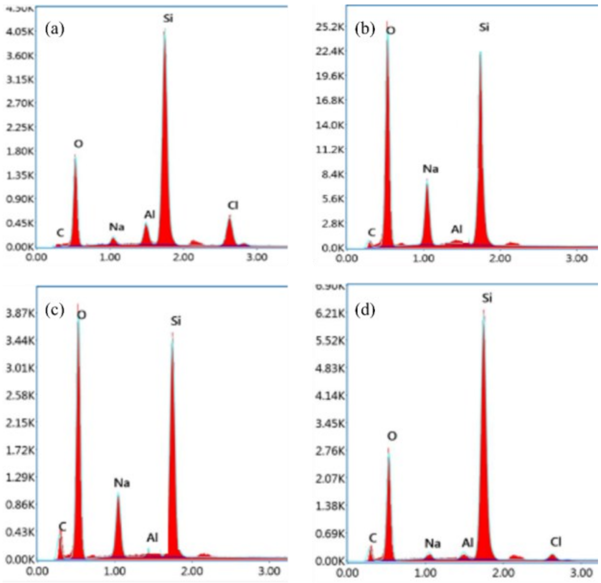


Figure 11. EDX spectra of silica xerogel at different volume ratios: (a) 0:1:1, (b) 1:1:1, (c) 2:1:1, and (d) 3:1:1

Table 3. EDX analysis of silica xerogel at different TMCS concentrations

Element	% Relative weight of elemental composition			
	Unmodified silica xerogel (0:1:1)	TMCS-modified silica xerogel		
		(1:1:1)	(2:1:1)	(3:1:1)
C	1.39	5.91	13.95	15.19
O	37.96	42.98	40.19	38.17
Na	2.14	13.28	11.74	1.81
Al	3.78	1.26	1.51	1.27
Si	45.55	36.56	32.61	41.51

Table 4. Surface area, total pore volume, and pore diameter of unmodified silica xerogel and TMCS-modified silica

Unmodified and TMCS-modified silica	BET surface area (m^2/g)	BJH pore diameter (nm)	BJH pore volume (cc/g)
0:1:1	11.795	7.556	0.03743
1:1:1	1.862	6.425	0.00150
2:1:1	1.648	3.392	0.00143
3:1:1	2.752	3.037	0.00234

The analysis also showed that the surface area of TMCS-modified silica xerogels is lower than that of the control silica xerogel. This reduction suggests that some pore structures may have collapsed during the drying process, causing partial damage to the porous network. Additionally, the simultaneous decrease in pore volume supports the possibility of pore blockage caused by the surface modification process.

3.3. Hydrophobicity Properties of Unmodified Silica Xerogel and TMCS-modified Silica

The contact angle measurements, presented in Figure 12 and Table 5, show that the hydrophobicity of silica xerogel increases with higher TMCS concentrations. This trend aligns with the FTIR results, where the absorption intensity of the Si–CH_3 groups increases as the TMCS concentration rises, indicating greater surface modification. The EDX analysis further supports these findings by confirming the increased presence of carbon from the trimethylsilyl groups. Together, these results demonstrate that TMCS modification effectively enhances the hydrophobicity of silica xerogel.

Table 5. Water contact angle value of unmodified and TMCS-modified silica xerogels

Silica xerogel volume ratio	Contact angle (°)
0:1:1 (unmodified)	99.325 ± 0.1
1:1:1	111.269 ± 0.2
2:1:1	121.449 ± 0.2
3:1:1	160.384 ± 0.1

Table 6. The adsorption capacity of unmodified and TMCS-modified silica xerogel at various oil concentrations in 50 mL of water

Adsorbent		Initial oil weight (g)	Oil concentration in water (C_0, mg/mL)	Equilibrium oil concentration (C_e, mg/L)	Absorbed oil concentration (q_e, mg/g)	C_e/q_e (g)
0:1:1	A	0	0	0	0	0
	B	0.02	0.4	0.009	11	0.001
	C	0.04	0.8	0.026	14	0.002
	D	0.06	1.2	0.0505	9.5	0.005
	E	0.08	1.6	0.0725	7.5	0.01
	F	0.1	2	0.094	6	0.016
1:1:1	A	0	0	0	0.5	0
	B	0.02	0.4	0.0025	17.5	0
	C	0.04	0.8	0.031	9	0.003
	D	0.06	1.2	0.054	6	0.009
	E	0.08	1.6	0.0675	12.5	0.005
	F	0.1	2	0.0775	12	0.006
2:1:1	A	0	0	0	0.5	0
	B	0.02	0.4	0.0065	13.5	0
	C	0.04	0.8	0.029	11	0.003
	D	0.06	1.2	0.054	6	0.009
	E	0.08	1.6	0.065	15	0.004
	F	0.1	2	0.082	18	0.005
3:1:1	A	0	0	0	0.5	0
	B	0.02	0.4	0	28.5	0
	C	0.04	0.8	0.0115	28.5	0
	D	0.06	1.2	0.043	17.0	0.003
	E	0.08	1.6	0.0635	16.5	0.004
	F	0.1	2	0.065	35	0.002

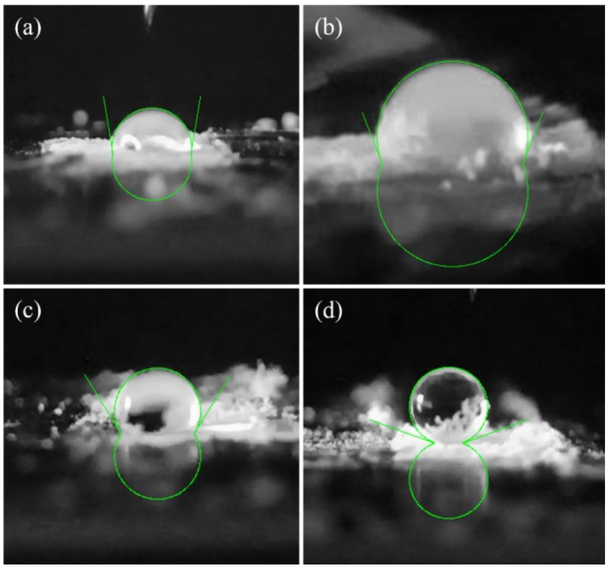


Figure 12. Contact angles of silica xerogel at different volume ratios: (a) 0:1:1, (b) 1:1:1, (c) 2:1:1, and (d) 3:1:1

3.4. Utilization of Unmodified and TMCS-modified Silica Xerogels for Oil Adsorption in Water

The TMCS-modified silica xerogel was further evaluated as an adsorbent for oil in water. The palm oil used in the experiments was packaged palm oil, primarily composed of palm oil triglycerides, along with vitamin A (containing the antioxidant tocopherol), Omega-6, Omega-9, and vitamin E. The results of the adsorption experiments with TMCS-modified silica xerogel are presented in Table 6. The maximum adsorption capacity was determined by calculating the amount of oil adsorbed, expressed in mg of oil per gram of adsorbent.

The adsorption equilibrium curves in Figure 13 exhibit a rapid increase in adsorption at low oil concentrations in water, followed by a gradual plateau as saturation is approached. To better understand the adsorption behavior, the adsorption parameters were calculated using both the Langmuir and the Freundlich isotherm models.

Table 7. Langmuir and Freundlich isotherm parameters

Adsorbent	Langmuir					Freundlich		
	Q_m (mg/g)	$K \times 10^{-3}$ (L/mol)	E (kJ/mol)	R^2	R_L	K_f (mg/g)	N	R^2
0:1:1	6.116	41.925	44.214	0.9669	1	1.335	1.805	0.872
1:1:1	6.381	57.401	45.006	0.9796	0.998	1.110	1.901	0.684
2:1:1	17.421	49.062	44.610	0.9512	0.994	1.177	1.519	0.643
3:1:1	22.472	570.535	50.791	0.805	0.993	4.274	1.951	0.310

Table 8. Comparison of oil adsorption performance using hydrophobic silica materials

Material	Precursor material	Adsorbate	Adsorption capacity	Reference
Silica aerogel – TEOS	Sodium silicate	Biodiesel	+ 45.26 cal/g (calorific value) –0.013 g/mL (density) + 0.934 (cSt) (viscosity) –9°C (flash point)	Oktavian *et al.* [11]
Silica aerogel – TMCS	Rice husk	Heavy metals in water	Cu^{2+} =33.4% Pb^{2+} = 96.9% Cd^{2+}= 10.5% Ni^{2+} = 2.5%	Hidayatulloh *et al.* [16]
Silica xerogel – TMCS	Fly ash	Oil in water	6–22 mg/g	This study

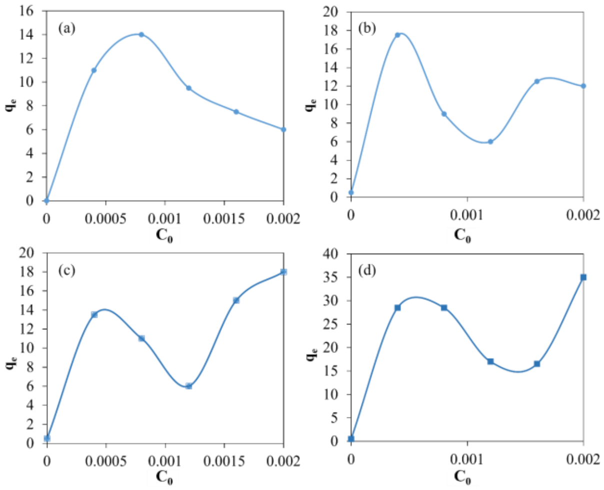


Figure 13. Equilibrium curves of oil adsorption in water on silica xerogel with volume ratios of (a) 0:1:1, (b) 1:1:1, (c) 2:1:1, and (d) 3:1:1

Based on Table 7, the Langmuir adsorption isotherm shows good linearity, indicating a strong fit with the experimental data. The maximum adsorption capacity (Q_m) increases with higher TMCS concentrations on the silica xerogel adsorbent, with the highest Q_m value of 22.472 mg/g observed for the 3:1:1 ratio. The adsorption behavior of the TMCS-modified silica xerogel predominantly follows the Langmuir isotherm, as evidenced by the correlation coefficient (R^2) being closer to 1 compared to the Freundlich model. Additionally, the R_L values from the Langmuir isotherm fall between 0 and 1 (ranging from 0.993 to 1), confirming that TMCS-modified silica xerogel is highly suitable for oil adsorption in water.

Based on Table 8, previous research using silica aerogel–TEOS material and sodium silicate showed certain limitations, particularly in the viscosity and flash point parameters, indicating that the improvement in biodiesel quality was not yet optimal. In another study, silica aerogel modified with TMCS and derived from rice husk exhibited the highest adsorption efficiency for Pb^{2+} ions at 96.9%, while the adsorption of other metal ions remained relatively low. In contrast, the present study on TMCS-modified silica xerogel synthesized from fly ash demonstrated a relatively high adsorption capacity for oil in water, with efficiency increasing in correlation with TMCS concentration.

4. Conclusion

Silica extracted from coal fly ash exhibits a purity of approximately 95%, as confirmed by XRF analysis. The extracted silica possesses an amorphous structure, indicated by a broad single peak at 2θ = 23.25° in the XRD pattern. Successful surface modification of silica xerogel with TMCS is evidenced by the appearance of Si–C and C– H vibrational bands in the FTIR spectra. Increasing the TMCS concentration enhances the hydrophobicity of the modified silica xerogel; however, it also results in a reduction in surface area. The TMCS-modified silica xerogel is classified as a mesoporous material, with pore diameters ranging from 3 to 7.5 nm. It exhibits a good adsorption capacity for oil in water, which increases with higher TMCS concentrations, achieving values between 6 and 22 mg/g.

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