

Article

Synthesis of Low Density and High Purity Silica Xerogels from South African Sugarcane Leaves without the Usage of a Surfactant

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Abstract: Sugarcane leaves were used to produce high-purity and low-density silica xerogels through a sol–gel method. The biogenic silica produced through a thermochemical method was reacted with sodium hydroxide (NaOH) to form sodium silicate and the produced sodium silicate was titrated with 1 M citric acid to form silica gel. The formed silica gel was washed, subjected to a solvent exchange process and later dried at 80 °C to produce low-density and high-purity silica xerogels. The produced xerogels were characterized with energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), nitrogen physisorption, elemental analysis (CHNS), X-ray fluorescence (XRF), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The produced silica xerogels had an amorphous structure and purity of 99.9 wt%. In addition, the textural properties analysis showed that the xerogel has a BET surface area of 668 m²·g^{−1}, an average pore diameter of 7.5 nm, a pore volume of 1.26 cm³·g^{−1} and a density of 0.23 g·cm^{−3}.

Keywords: xerogel; sugarcane leaves; sol–gel method; amorphous biogenic silica; value added material; solvent exchange



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1. Introduction

Sugarcane leaves are an agricultural waste material that is produced in very high amounts in countries that plant sugarcane [1]. Therefore, the usage of sugarcane leaves can yield a value-added material such as biogenic silica. Biogenic silica, obtained through the thermochemical treatment of sugarcane leaves, has been reported to yield silica with a high purity when either a mineral or organic acid is utilized in its treatment [1]. Through further treatment of biogenic silica, a silica product with higher purity and textural properties can be successfully produced [2].

Classical silica gel is produced through the gelation and ageing of a colloidal silica sol, which is commonly formed by an alkoxide precursor such as tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS) [3]. An alternative and relatively less expensive method of producing high-purity silica was reported by Kalapathy et al. [4], where silica ash was dissolved in an alkaline solution such as sodium hydroxide to form sodium silicate; this subsequently resulted in an aqua gel through the addition of an acid. The aqua gel was further aged, washed and dried to produce a silica aerogel or xerogel [5], depending on the aim of the study.

Silica aerogels are mainly mesoporous solids that comprise of a three-dimensional nanoparticle network with mesopores that are interstitial [3]. They are known to consist a range of utmost material properties [3]. They have various industrial applications due to their low density, high porosity, high surface-area-to-volume ratio, simple and flexible surface modification, high thermal stability and good insulation ability [6]. These types of silica gels are synthesized through a sol–gel method in which the produced gel needs to be dried through supercritical drying conditions. This, however, becomes problematic in large-scale industrial productions due to the high costs and danger involved in working at a high temperature and pressure during the supercritical drying process [6].

As a result, intensive research on the synthesis of xerogels on a large scale has been carried out over the years. Several researchers have utilized different low-cost xerogel precursors, such as rice husk [4], fly ash [7], kaolin [8] and oil shale ash [9], for the production of xerogels. Both xerogels and aerogels are prepared through the same sol–gel method; the only major difference is the way the resulting gel is treated/dried. Xerogels are less energy intensive because they are dried at low temperatures and ambient pressures [10]. Silica xerogels can be used in several applications, such as the following: thermal insulators, absorbents in the removal of fatty acids, oxidation products in oil and filtering media during water purification or of organic solvents [11]. They can also be used as chromatography columns and catalyst supports [12]. Among numerous drug delivery materials in the medical field, there has been an increasing interest in silica-based materials due to their biocompatible, nontoxic and stable nature [13]. Czarnobaj et al. [13] reported that, at the state of liquid sol, drug molecules can be readily loaded into the matrix without compromising the integrity of the drug. The drug molecules entrapped within the matrix are able to retain their physical characteristics and their biological and chemical properties within the silica material [13].

Several parameters, such as the solvent composition, chemical precursor, temperature and pH, have been reported by Estella et al. [14] to affect condensation and hydrolysis reactions; these, in turn, affect the porosity of silica xerogels. In addition, the washing step of the gel is crucial as it strongly determines the purity of the final product and its surface adsorption properties [4]. According to Kalapathy et al. [4], additional washing might be required after drying the gel in an attempt to produce a gel with lesser impurities. Silica xerogels that are pure or contain less impurities have a unique advantage because they can be used in applications that do not tolerate the presence of inorganic impurities. An example of such an application is the pharmaceutical industry, where they can be used as drug carriers.

Herein, we report the synthesis of high-quality silica xerogels from sugarcane leaves, which are regarded as a waste in the sugar production industry. The main purpose of this study was to produce silica with high-purity, low-density and good porous properties through a sol–gel method without the usage of a surfactant. Another batch of silica xerogel was produced using a surfactant (poly vinyl alcohol (PVA)) for comparison purposes. The xerogel produced in this study had improved properties compared to the biogenic silica that was produced in a previous study through a thermochemical route reported by Maseko et al. [1]. The xerogels reported in this study have superior properties, such as higher purity, a low density and better textural properties. Such characteristics make it possible for this silica xerogel to be used in a wide range of applications such as the ones mentioned above. This study further demonstrates that the method utilized produced silica xerogels from sugarcane leaves that have excellent properties in the absence of either a surfactant or harsh inorganic acids; these are still highly comparable to its counterparts in the literature, which were produced in the presence of a surfactant and strong mineral acids, which are environmentally unfriendly. To the best of our knowledge, no work has been published in the literature that utilized biogenic silica from sugarcane leaves in the production of silica xerogels by hydrolyzing sodium silicate with citric acid in the absence of a surfactant. In addition, this method

further employed an ethanol solvent exchange method to increase textural properties and, in turn, enhance other properties, such as the density.

2. Materials and Methods

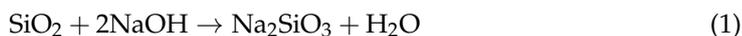
2.1. Materials

Citric acid, sodium hydroxide, poly vinyl alcohol (PVA) and absolute ethanol were purchased from Merck (South Africa). Sugarcane leaves were obtained from sugarcane growers in Verulam, South Africa.

2.2. Methods

2.2.1. Experimental

Biogenic silica was synthesized using a method reported by Maseko et al. [1]. In a 3-neck round-bottom flask, 5 g of biogenic silica was mixed with 250 mL of 1 M sodium hydroxide and the mixture was refluxed for 2 h at 80 °C. The resulting sodium silicate solution was then cooled to room temperature and later filtered to remove any present undigested matter. In a 500 mL beaker, the prepared sodium silicate solution was hydrolyzed with the addition of 1 M citric acid until the solution turned turbid at a pH of around 8.7. The formation of silica gel occurred according to the following reactions (1) and (2):



After the solution turned turbid, it was continuously stirred for about a minute more until the solution turned into a soft gel. Then, the magnetic stirrer was removed and the gelled solution was covered with parafilm and left to age for 8 h at room temperature. After 8 h, the gel was broken, washed with distilled water and centrifuged five times to remove any present sodium citrate salt. Water solution was then added into the washed gel in different ratios (1:3, 1:1 and 1:0) and was left overnight in each of the solution ratios to stimulate solvent exchange where water molecules are eventually replaced by ethanol molecules. After solvent exchange, the gel was dried in the oven at 80 °C for 24 h. The sample was removed from the oven and labelled Xe-No surfactant. In another reaction, 250 mL of the same filtered sodium silicate solution was placed in a 500 mL beaker and 5 mL of 5 wt% PVA was added to the solution; the mixture was then stirred for 30 min before being titrated by 1 M citric acid until the solution turned turbid. After the solution turned turbid, it was continuously stirred for about a minute more until a soft gel formed. The soft gel (aqua gel) was then covered with parafilm and left to age for 8 h. After 8 h, the gel was broken then washed with distilled water and centrifuged 5 times to remove any present sodium citrate salt. Subsequently, the surfactant was removed from the prepared silica xerogels using a method reported by Jabariyan et al. [15]. The gel was later dried in the oven at 80 °C for 24 h. The sample was then removed from the oven and labelled Xe-PVA. This method was followed exactly as reported in order to achieve the complete removal of PVA from silica xerogel. Figure 1 illustrates the synthesis procedure for both routes.

FTIR spectra were attained using a Nicolet Avatar 360 FTIR spectrometer (Madison, WI, USA). For each sample, 32 scans in the 4000–400 cm^{-1} spectral range were recorded. Nitrogen sorption measurements were performed to measure textural properties using ASAP 2010, Micromeritics, Norcross, 157 GA (USA). The chemical analysis was conducted through an X-ray fluorescence analysis (S4 Explorer, WDXRF Bruker, Karlsruhe, Germany). An elemental analysis was carried out using a Vario EL micro analyzer system (Heraeus, Hanau, Germany). Scanning electron microscopy (SEM) and Energy Dispersive X-ray (EDX) images were obtained on a Zeiss Ultra Plus FEG SEM (Oberkochen, Germany), and TEM images were obtained from the usage of JEOL 2100 HRTEM (Japan). The phase identification was measured using a Seifert XRD 7 apparatus that is equipped with Ni-149-filtered Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$).

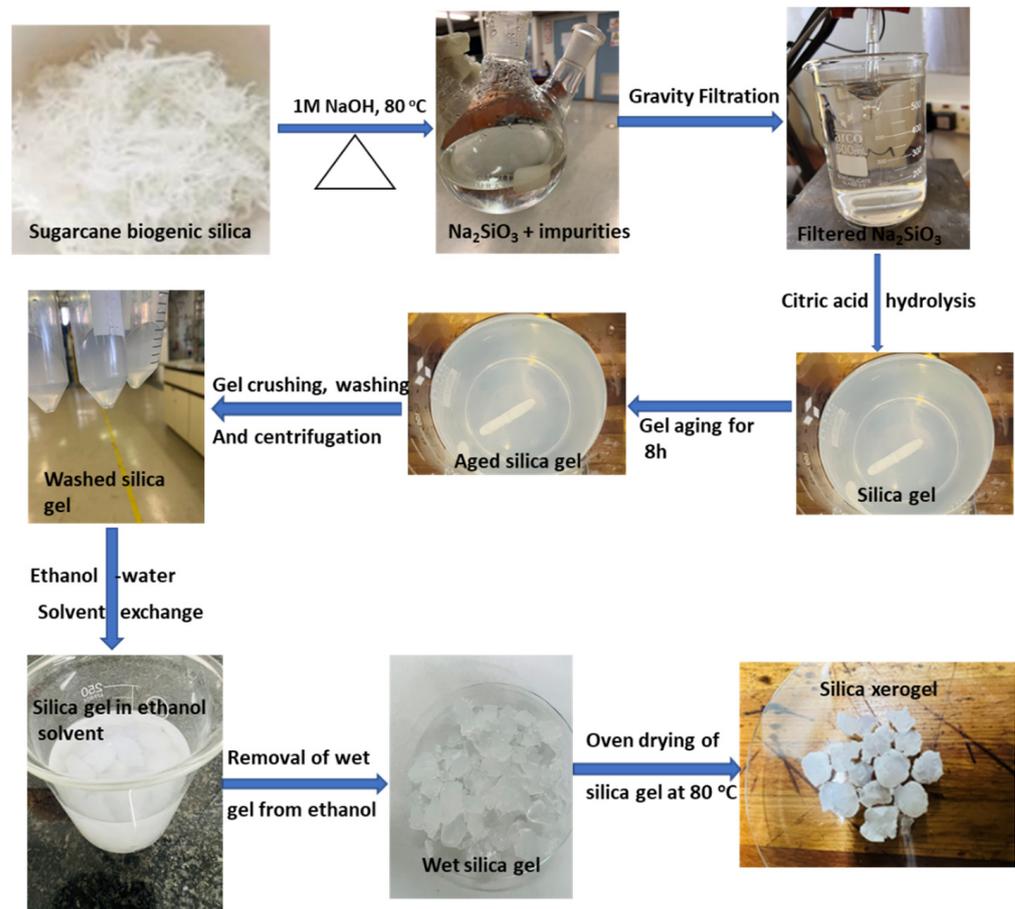


Figure 1. Schematic diagram for the synthesis of silica xerogels from sugarcane leaves biogenic silica.

2.2.2. Characterization of Silica Xerogels

3. Results and Discussion

3.1. FTIR Analysis of the Silica Xerogels

Figure 2 shows the FTIR spectra of silica xerogels that were produced from both gels. The broad peak at around 3410 cm^{-1} corresponds to the absorbed water and -OH stretching vibrations associated with silanol groups. All samples were kept in a desiccator but silica xerogels have been reported by [16,17] to be hygroscopic in nature. According to Darmakkolla et al. [17], silica xerogels are best kept in inert atmospheres to prevent the possibility of the reabsorption of ambient moisture, which will result in the presence of this peak at around 3410 cm^{-1} . The absorption bands around 1635 cm^{-1} represent the -OH groups from water molecules that are physically absorbed in the network. The most prominent peak at around 1070 cm^{-1} corresponds to the asymmetric vibrations of siloxane groups (Si-O-Si) [18], while the peaks around 950 cm^{-1} correspond to the Si-OH stretching vibrations [19]. The symmetric vibrations of Si-O-Si are presented by the peaks at 795 cm^{-1} [5]. The peak at around 460 cm^{-1} is associated with the bending vibrations of Si-O-Si. The peaks related to PVA were not observed in the spectrum of Xe-PVA, indicating its successful removal.

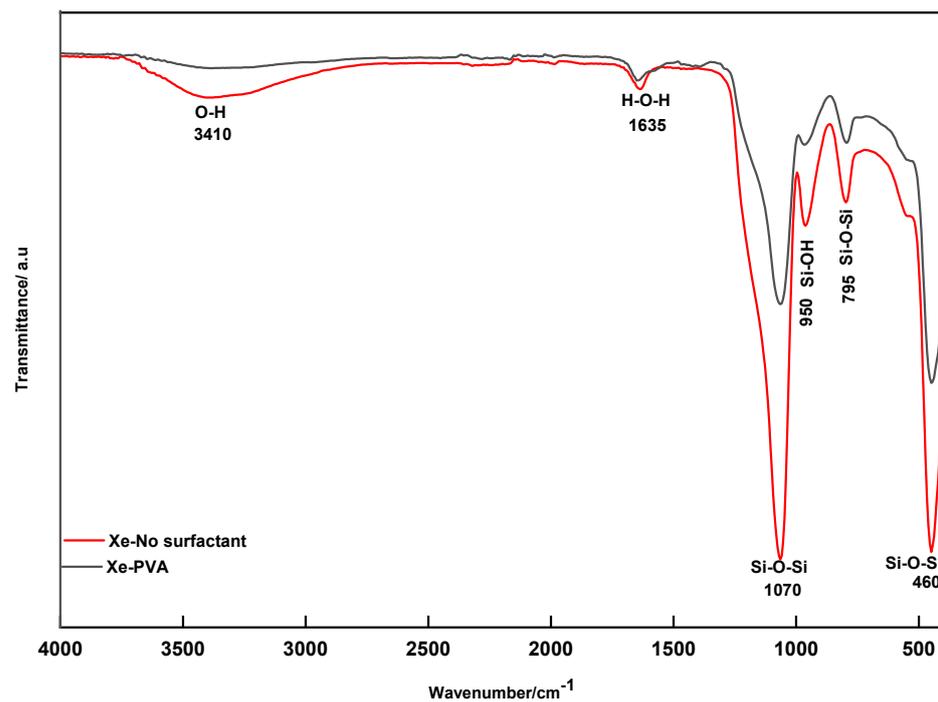


Figure 2. FTIR spectra for Xe-No surfactant and Xe-PVA xerogels.

3.2. XRD Analysis

The identification of possible different phases produced during the synthesis of silica xerogel from biogenic silica was performed by the means of XRD analysis and the results are displayed in Figure 3. Both of the samples exhibited only one broad peak at 21.9° and this peak is associated with amorphous silica [20]. No other peaks were observed in the xerogel samples, which means that the samples were completely amorphous, with undetected traces of crystalline phases. This was expected, since amorphous biogenic silica was utilized. According to Blond et al. [21], silica only begins to form a crystalline phase at temperatures above 900°C and the maximum temperature used in this work was 80°C .

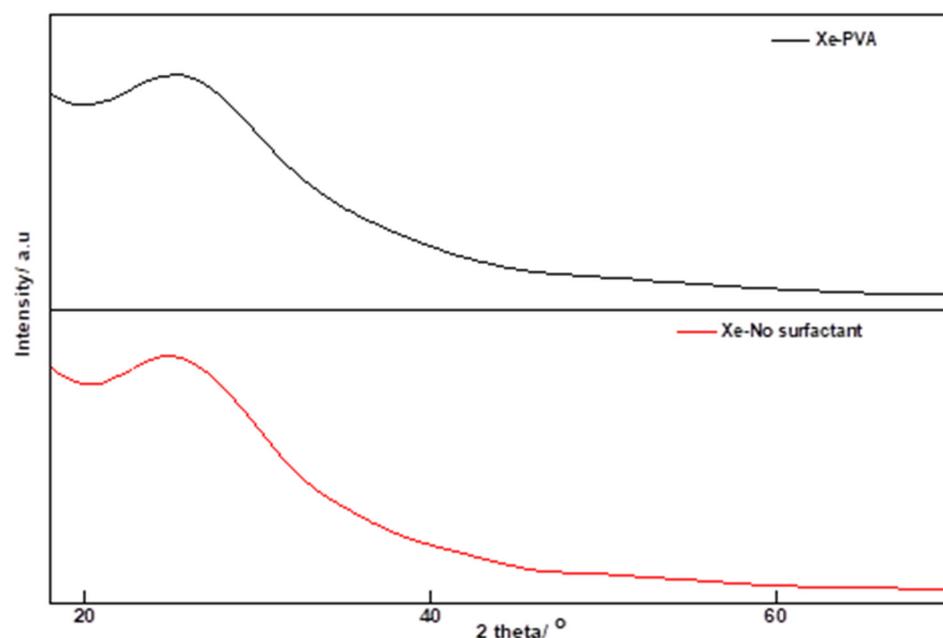


Figure 3. XRD pattern of Xe-PVA and Xe-No surfactant.

3.3. Properties of the Pore System

Figure 4 demonstrates the isotherms for silica xerogels that were obtained through nitrogen sorption characterization. The isotherms have a closed hysteresis loop and comprise a knee at $p/p_0 = 0.6$, which is immediately followed by a nitrogen uptake that is continuous until high relative pressure values [1]. These types of isotherms are categorized as type IV and are known to show low adsorption at low relative pressures, which is followed by a rapid increase at higher relative pressures [13]. According to Liu et al. [22], this is characteristic of mesoporous solids, which are known to have a pore diameter that is greater than 2 nm as per the IUPAC recommendation. Both silica xerogel samples followed the same type IV isotherm pattern, and their hysteresis loops have a slightly higher closure point at a relative pressure of 0.6; this can be classified as H2 [23]. The obtained hysteresis loop in the isotherms is due to the existence of larger mesopores [24]. No saturation is observed at relative pressure ratios close to unity, which means that the xerogel samples contain both meso- and macropores with a broad size distribution [25]. Based on the obtained isotherms, none of them reached a plateau at high values of p/p_0 . According to Schneider et al. [26] and Kumar et al. [27], an incomplete pore filling by an adsorbate took place, thereby suggesting that larger meso- and macropores were present in the xerogels.

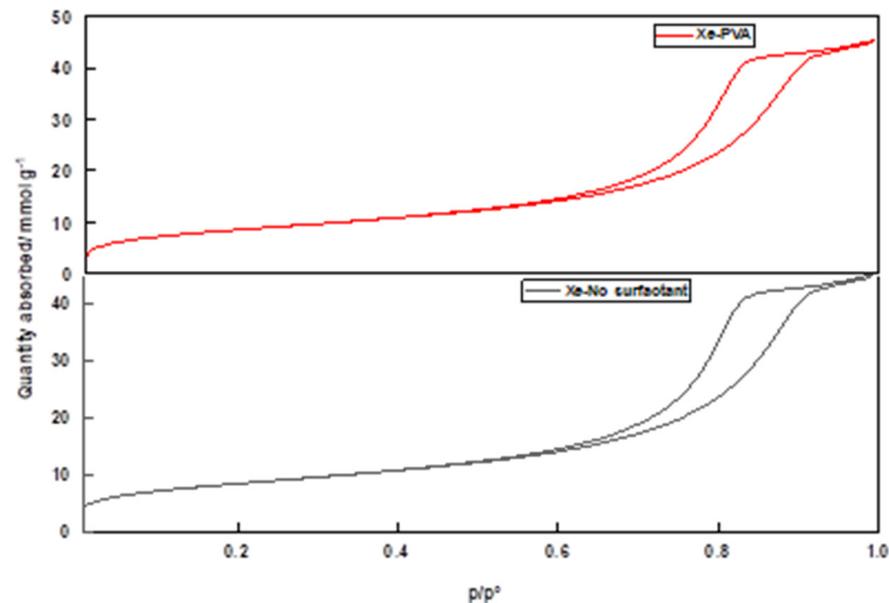


Figure 4. Nitrogen sorption isotherms of silica xerogels produced from sugarcane leaves with and without a surfactant.

The textural properties of the produced silica xerogels, such as BET surface area, pore diameter and pore volume, are summarized in Table 1. The method used to synthesize xerogels and the reaction conditions, such as the pH, synthesis temperature, aging time, drying temperature, washing method and time, strongly affect the textural properties of the produced xerogels. Optimized reaction conditions are considered in this study for the synthesis of silica xerogels in order to obtain the possible highest surface area and pore volume.

Table 1. Textural properties of produced silica xerogels determined by nitrogen sorption.

Sample	A_{BET} $\text{m}^2 \text{g}^{-1}$	Pore Diameter (nm)	Pore Volume $\text{cm}^3 \text{g}^{-1}$
Xe-No surfactant	668	7.5	1.25
Xe-PVA	693	9.2	1.61

Table 2 demonstrates the results that other researchers obtained from their synthesis of silica xerogels or silica nanoparticles through the sol–gel method. The xerogel that was prepared in the absence of a surfactant had a BET surface area of $668 \text{ m}^2 \cdot \text{g}^{-1}$, while the one that was prepared with PVA as a surfactant had a BET surface area of $693 \text{ m}^2 \cdot \text{g}^{-1}$, which is 3.7% more. Both of these surface areas are higher than most of the ones that were found in the literature and are quite comparable to silica xerogel produced from a TMOS and TEOS of 670 and $697 \text{ m}^2 \cdot \text{g}^{-1}$, respectively; these are well-known silica gel precursors with well-established production methods. However, Purnawira et al. [28] reported silica xerogel with a BET surface area of $768 \text{ m}^2 \cdot \text{g}^{-1}$, using rice husk as a silica precursor and CTAB as a surfactant. The surface area obtained by these researchers is 10% higher than the one found in this study; however, the aim of their study was to form mesoporous silica nanoparticles of the MCM-41 type, which is a slightly different material from the xerogel produced in this study. The pore diameter of the silica xerogel produced without a surfactant was found to be 7.5 nm , which is approximately 22% less than 9.2 nm , which is the quantity of silica xerogel produced when using PVA as a surfactant. Both of these pore diameters corroborate the results obtained from nitrogen sorption isotherms, which demonstrated the presence of mesopores. Kaya et al. [6] reported a comparable pore diameter of 10 nm for SiO_2 , which was obtained from volcanic tuff without any usage of a surfactant; however, these researchers' BET surface area was only $197 \text{ m}^2 \cdot \text{g}^{-1}$. The pore volume of xerogel produced without any surfactant was $1.25 \text{ cm}^3 \cdot \text{g}^{-1}$, which is 29% less than that of xerogel produced in the presence of a surfactant. Both the obtained pore volumes from this study are higher than the ones reported by researchers who have produced silica gel-based products. To the best of our knowledge, all the textural properties of the silica xerogels produced through a sol–gel method reported in the literature, with a higher surface area than the ones obtained in this study, were achieved through the utilization of a surfactant [28,29]. It is also worth mentioning that mineral acids were used to produce the gel in most of the work reported in Table 2, as opposed to the usage of an organic acid in this study. It can be summarized that the sample Xe-No surfactant had one of the highest BET surface areas of the porous silica materials synthesized on the basis of a biogenic silica source; this was also without a surfactant and using an organic acid as a catalyst in the sol–gel process via a completely sustainable route.

Table 2. Porous silica xerogel properties from the literature.

Source of Silica Surfactant Used	BET Surface Area $\text{m}^2 \cdot \text{g}^{-1}$	Pore Diameter (nm)	Pore Volume $\text{cm}^3 \cdot \text{g}^{-1}$	Reference
TEOS—NA	441	2.2	0.36	Yingyu Guo [30]
TMOS—NA	670	4.9	0.73	Czarnobaj et al. [13]
TEOS—NA	697	nr	0.42	Estella [14]
volcanic tuff—None	197	10.0	0.50	Kaya [6]
Rice husk—CTAB	768	6.1	1.17	Purnawira et al. [28]
Salacca Leaf—None	93	1.2	0.03	Fatimah et al. [2]
Rice husk—CTAB	706	5.81	1.03	Purwaningsih et al. [29]
Palm kernel—None	438	2.2–6.3	nr	Imoisili et al. [31]
Corn cob—None	57	4.7	0.67	Shim et al. [20]
Corn husk—None	384	3.8	0.35	Prempeh et al. [32]
Rice husk—None	653	2.0	0.65	Hassan [33]
Sugarcane waste ash—None	131	2.2	1.05	Rovani et al. [18]
Sugarcane bagasse—None	137	3.4	0.14	Affandi et al. [34]
Sugarcane bagasse—P123	466	3.1	0.14	Norsuraya et al. [35]

NA = Not Applicable, nr = Not Reported.

The density of the xerogels was determined by filing the gel to a perfect rectangle and then using a Vernier caliper to measure its sides so that its volume could be determined. The mass of the same xerogel rectangle was determined and its density was then calculated from $\rho = \frac{m}{v}$. The xerogel prepared in the absence of a surfactant was found to have a

density of $0.23 \text{ g}\cdot\text{cm}^{-3}$, while that of the xerogel prepared in the presence of a surfactant was found to be slightly lower at $0.19 \text{ g}\cdot\text{cm}^{-3}$.

3.4. Elemental Analysis

Elemental analysis of the xerogel samples was carried out to determine any present carbon, nitrogen, hydrogen and sulfur (Table 3). The results obtained established that both the xerogel samples had neither carbon nor sulfur present, and had low percentages (less than 0.1%) of both hydrogen and nitrogen. These results agree with EDX analysis (Figure 5), which reflected that neither carbon nor sulfur were present in the xerogels. Both these elements were below the detection limits.

Table 3. Elemental analysis (CHN) for xerogel samples synthesized from sugarcane leaves.

Xerogel	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulphur (%)
Xe-No surfactant	n.d	0.09 ± 0.01	0.01 ± 0.00	n.d
Xe-PVA	n.d	0.07 ± 0.01	0.01 ± 0.01	n.d

n.d = not detected.

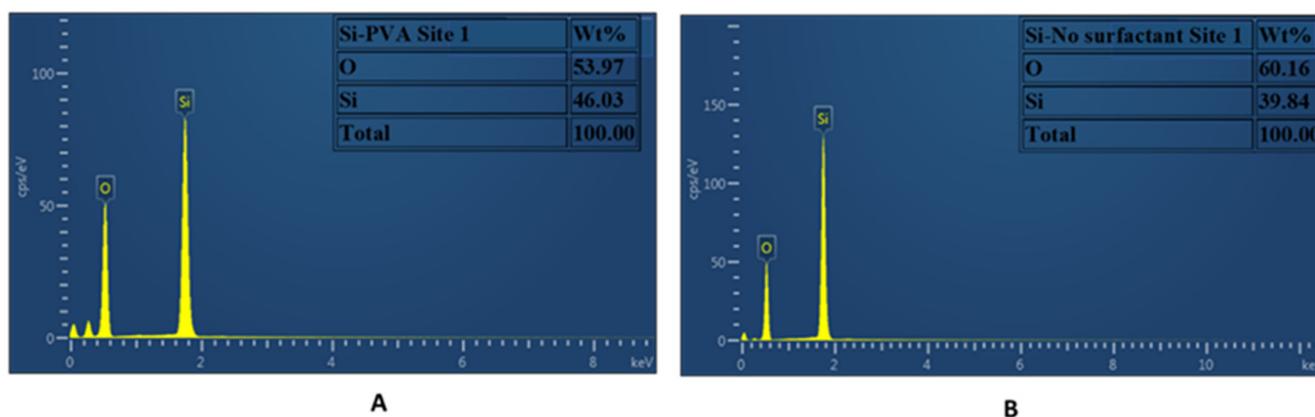


Figure 5. EDX spectra of xerogel produced from sugarcane leaves. (A) Xe-PVA, (B) Xe-No surfactant.

An XRF analysis was conducted to study the chemical composition of the xerogels produced and the biogenic silica that was used to prepare the gels; the results are displayed in Table 4. It can be observed that all the other inorganic impurities that were present in the biogenic silica reported in the previous study by Maseko et al. [1] were removed to beyond the detection limit in the xerogels, except for K_2O and CaO . The reduction for K_2O and CaO was 95% and 98%, respectively, for Xe-No surfactant. Meanwhile, for Xe-PVA, K_2O and CaO were reduced by 70% and 95%, respectively. The obtained purity through XRF analysis of the produced Xe-No surfactant was 99.9 wt%, while that for Xe-PVA was 99.8 wt%. The biogenic silica used to prepare the gels had a purity of 95.4 wt%. The purity of the biogenic silica was improved by approximately 4.5% for both the Xe-No surfactant and Xe-PVA that were synthesized in this study.

Researchers such as Setyawan et al. [36] and Prempeh et al. [32] reported a presence of more than 5 wt% of Na_2O in their xerogel product. It is worth noting that even though sodium citrate was formed as a by-product during the xerogel synthesis, no sodium was detected in the final product. The absence of sodium was achieved through the sufficient washing of the gels; the gels were washed 5 times and were shaken/agitated by hand every time before they were placed into a centrifuge for the separation of the gel and the liquid. The gels were later subjected to solvent exchange.

Table 4. Chemical analysis of sugarcane leaves biogenic silica, Xe-No surfactant and Xe-PVA (determined by XRF).

Constituent	Biogenic Silica (wt%)	Xe-No Surfactant (wt%)	Xe-PVA (wt%)
SiO ₂	95.4	99.9	99.8
Fe ₂ O ₃	0.2	n.d	n.d
P ₂ O ₅	0.4	n.d	n.d
K ₂ O	0.2	0.01	0.06
CaO	2.6	0.05	0.12
MgO	0.4	n.d	n.d
SO ₃	0.9	n.d	n.d
Al ₂ O ₃	0.1	n.d	n.d
Others ^a	0.0	0.0	0.0

n.d: not detected, Others^a: other metal oxides.

Figure 5 shows the results obtained from EDX analysis of the silica xerogel, where Figure 5A represents Xe-PVA and Figure 5B represents the Xe-No surfactant. It can be observed that both the purity of the Xe-no surfactant and Xe-PVA was quite high, with no carbon detected. These results agree with CHNS analysis, since no carbon is reported to be present or significant.

3.5. SEM and TEM Analysis

Scanning electron microscopy (SEM) was used to study the surface morphology of the produced xerogels and to determine any possible surface modifications that might have occurred due to the usage of a surfactant. The results are presented in Figure 6. Figure 6A,B show the Xe-No surfactant and Xe-PVA, respectively, at high magnification. Both of the presented SEM images demonstrate aggregation, which is caused by the presence of nanoparticles in the gels, as reported through nitrogen sorption. Figure 6C,D show the Xe-No surfactant and Xe-PVA, respectively, at lower magnification, and both of these images illustrate that the produced gels consist of particles with different sizes and shapes accompanied by some aggregation. According to [37], the type of silica produced in this study is known as heterogenous mesopore silica. Figure 6C,D further indicate that the produced xerogels have a rough and amorphous surface [38]. Amorphous silica is represented by the brighter surfaces while the pore cavities are indicated by the darker surfaces [37]. These findings support the results obtained through nitrogen sorption, where both of the synthesized xerogels were type IV silica with a mesoporous structure.

TEM images of the silica xerogels are presented in Figure 7A,B for the Xe-No surfactant and Xe-PVA, respectively. It can be seen that both xerogels produced silica particles that have no defined shape, with some agglomeration present. At this length scale, the small nanoparticles are most likely to agglomerate and form mesopores, as observed by nitrogen sorption. However, the degree of agglomeration for Xe-PVA is lower than that of the Xe-No surfactant, and also Xe-PVA appears to have larger pores than the Xe-No surfactant. This observation is in agreement with the results obtained from N₂-sorption, since the reported pore diameters of Xe-PVA and the Xe-No surfactant are 9.2 nm and 7.5 nm, respectively. There is no regular geometry that can be confirmed, and this corroborates the amorphous nature of the produced silica gels, as detected by XRD [39].

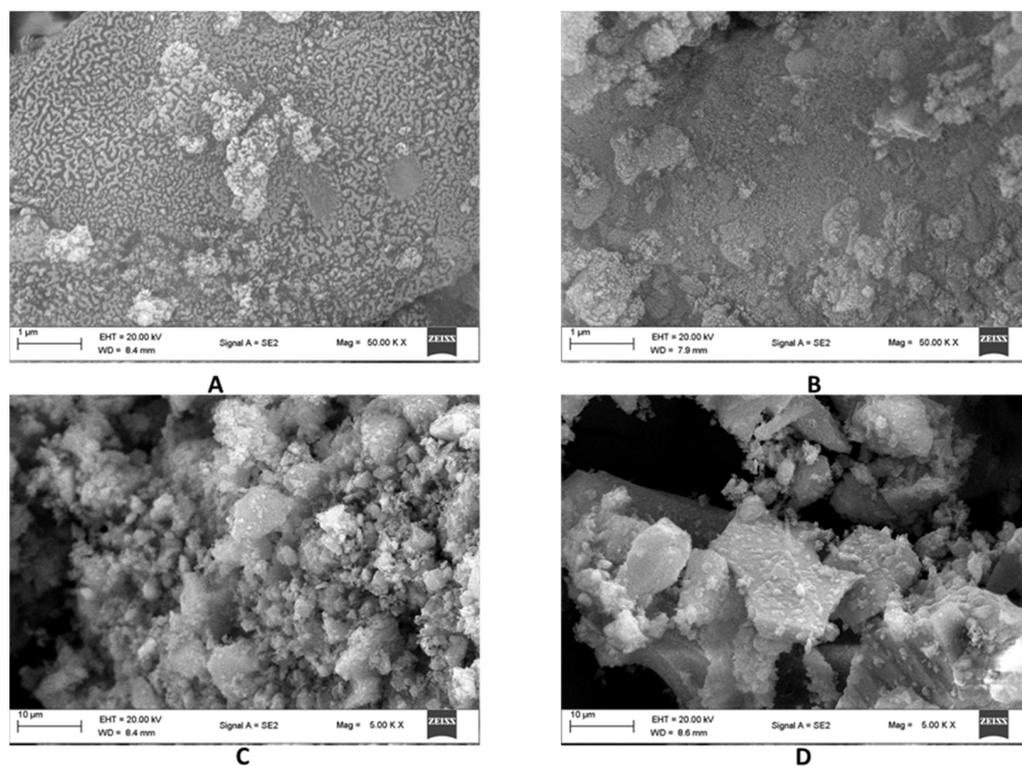


Figure 6. SEM images for silica xerogel from sugarcane leaves. (A) Xe-No surfactant (high magnification), (B) Xe-No surfactant (high magnification), (C) Xe-No surfactant (low magnification) and (D) Xe-PVA (low magnification).

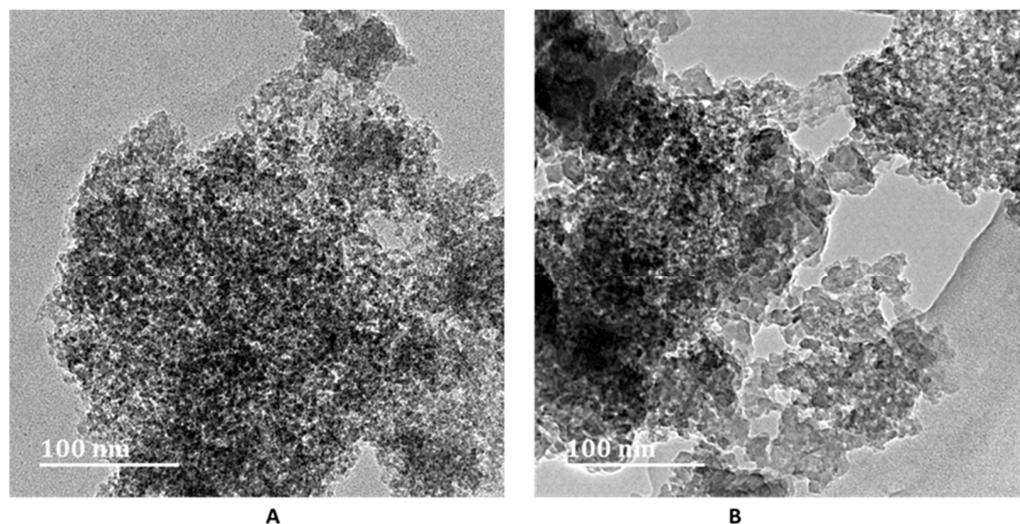


Figure 7. TEM images of silica xerogels from sugarcane leaves. (A) Xe-No surfactant and (B) Xe-PVA.

4. Conclusions

This study demonstrated the synthesis of porous silica without the usage of a surfactant, which always requires an extra removal step. The results showed that silica xerogel, with a high purity of up to 99.9 wt% and also a low density of $0.23 \text{ g}\cdot\text{cm}^{-3}$, can be obtained through the sol–gel method, coupled with gradual solvent exchange between water and ethanol. The xerogel produced was completely amorphous, its particles had different shapes and sizes, and it was almost free of impurities. The synthesized silica xerogel had very good pore system properties, with a BET surface area of $668 \text{ m}^2\cdot\text{g}^{-1}$, pore diameter of 7.5 nm and pore volume of $1.25 \text{ cm}^3\cdot\text{g}^{-1}$. Specific and consistent aging times, washing and solvent exchange times were used to ensure precision.

Author Contributions: Conceptualization, N.N.M.; methodology, N.N.M.; validation, N.N.M., D.E. and S.A.I.; investigation, N.N.M.; data curation, N.N.M.; writing—original draft preparation, N.N.M.; writing—review and editing, S.A.I., D.E., O.S.O. and J.P.; visualization, N.N.M., S.A.I. and D.E.; supervision, J.P., S.A.I. and O.S.O.; funding acquisition, University Capacity Development Program. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Maseko, N.N.; Schneider, D.; Wassersleben, S.; Enke, D.; Iwarere, S.A.; Pocock, J.; Stark, A. The production of biogenic silica from different South African agricultural residues through a thermo-chemical treatment method. *Sustainability* **2021**, *13*, 577. [[CrossRef](#)]
2. Fatimah, I.; Zaenuri, F.U.; Doewandono, L.N.; Yahya, A.; Citradewi, P.W.; Sagadevan, S.; Oh, W.-C. Biogenic Silica Extracted from Salacca Leaf Ash for Salicylic Acid Adsorption. *Sci. Technol. Indones.* **2021**, *6*, 296–302. [[CrossRef](#)]
3. Iswara, S.; Malfaita, W.J.; Balogb, S.; Winnefeldc, F.; Lattuadab, M.; Koebela, M.M. Effect of aging on silica aerogel properties. *Microporous Mesoporous Mater.* **2017**, *241*, 293–302. [[CrossRef](#)]
4. Kalapathy, U.; Proctor, A.; Shultz, J. An improved method for production of silica from rice hull ash. *Bioresour. Technol.* **2002**, *85*, 285–289. [[CrossRef](#)]
5. Al-Oweini, R.; El-Rassy, H. Synthesis and characterization by FTIR spectroscopy of silica aerogels prepared using several Si(OR)₄ and R''Si(OR')₃ precursors. *J. Mol. Struct.* **2020**, *919*, 140–145. [[CrossRef](#)]
6. Kaya, G.; Yilmaza, E.; Devecia, H. A Novel Silica Xerogel Synthesized from Volcanic Tuff as an Adsorbent for High Efficient Removal of Methylene Blue: Parameter Optimization Using Taguchi Experimental Design. *J. Chem. Technol. Biotechnol.* **2019**, *94*, 2729–2737. [[CrossRef](#)]
7. Li, Z.-D.; Wang, H.-L.; Wei, X.-N.; Liu, X.-Y.; Yang, Y.-F.; Jiang, W.-F. Preparation and photocatalytic performance of magnetic Fe₃O₄@TiO₂ core-shell microspheres supported by silica aerogels from industrial fly ash. *J. Alloys Compd.* **2016**, *659*, 240–247. [[CrossRef](#)]
8. Hu, W.; Li, M.; Chen, W.; Zhang, N.; Li, B.; Wang, M.; Zhao, Z. Preparation of hydrophobic silica aerogel with kaolin dried at ambient pressure. *Colloid. Surf. A Physicochem. Eng. Asp.* **2016**, *501*, 83–91. [[CrossRef](#)]
9. Gao, G.-M.; Liu, D.-R.; Zou, H.-F.; Zou, L.-C.; Gan, S.-C. Preparation of silica aerogel from oil shale ash by fluidized bed drying. *Powder Technol.* **2010**, *197*, 283–287. [[CrossRef](#)]
10. Vareda, J.P.; Durães, L. Functionalized silica xerogels for adsorption of heavy metals from groundwater and soils. *J. Sol-Gel Sci. Technol.* **2017**, *84*, 400–408. [[CrossRef](#)]
11. Kalapathy, U.; Proctor, A.; Shultz, J. Silica xerogels from rice hull ash: Structure, density and mechanical strength as affected by gelation pH and silica concentration. *Chem. Technol. Biotechnol.* **2000**, *75*, 464–468. [[CrossRef](#)]
12. Kalapathy, U.; Proctor, A.; Shultz, J. A simple method for production of pure silica from rice hull ash. *Bioresour. Technol.* **2000**, *73*, 257–262. [[CrossRef](#)]
13. Czarnobaj, K.; Sawicki, W. Influence of surfactants on the release behaviour and structural properties of sol-gel derived silica xerogels embedded with metronidazole. *Pharm. Dev. Technol.* **2013**, *18*, 377–383. [[CrossRef](#)] [[PubMed](#)]
14. Estella, J.; Echeverria, J.; Laguna, M.; Garrido, J. Effects of aging and drying conditions on the structural and textural properties of silica gels. *Microporous Mesoporous Mater.* **2007**, *102*, 274–282. [[CrossRef](#)]
15. Jabariyan, S.; Zanjanchi, M.A. A simple and fast sonication procedure to remove surfactant templates from mesoporous MCM-41. *Ultrason. Sonochemistry* **2012**, *19*, 1087–1093. [[CrossRef](#)]
16. De Vasconcelos, A.B.P.; Silva, W.E.; Belian, M.F. PH dependent drug delivery based on silica xerogel. *J. Chil. Chem. Soc.* **2017**, *62*, 3700–3702. [[CrossRef](#)]
17. Darmakkolla, S.R.; Trana, H.; Gupta, A.; Blackwell, J.; Ranavavare, S.B. A method to derivatize surface silanol groups to Si-alkyl groups in carbon-doped silicon oxides. *R. Soc. Chem. Adv.* **2016**, *6*, 93219–93230. [[CrossRef](#)]
18. Rovani, S.; Santos, J.J.; Corio, P.; Fungaro, D.A. Highly Pure Silica Nanoparticles with High Adsorption capacity obtained from Sugarcane Waste Ash. *ACS Omega* **2018**, *3*, 2618–2627. [[CrossRef](#)] [[PubMed](#)]
19. Li, M.; Jiang, H.; Xu, D.; Hai, O.; Zheng, W. Low density and hydrophobic silica aerogels dried under ambient pressure using a new co-precursor method. *J. Non-Cryst. Solids* **2016**, *452*, 187–193. [[CrossRef](#)]
20. Shim, J.; Velmurugan, P.; Oh, B.-T. Extraction and physical characterization of amorphous silica made from corn cob ash at variable pH conditions via sol gel processing. *J. Ind. Eng. Chem.* **2015**, *30*, 249–253. [[CrossRef](#)]
21. Blond, J.S.L.; Horwell, C.J.; Williamson, B.J.; Oppenheimer, C. Generation of crystalline silica from sugarcane burning. *J. Environ. Monit.* **2010**, *12*, 1459–1470. [[CrossRef](#)] [[PubMed](#)]

22. Liu, G.; Yang, R.; Li, M. Liquid adsorption of basic dye using silica aerogels with different textural properties. *J. Non-Cryst. Solids* **2010**, *356*, 250–257. [[CrossRef](#)]
23. Thommes, M.; Kanelo, K.; Neimark, A.; Olivier, J.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87*, 1051–1069. [[CrossRef](#)]
24. Alyosef, H.A.; Schneider, D.; Wassersleben, S.; Roggendorf, H.; Weiß, M.; Eilert, A.; Denecke, R.; Hartmann, I.; Enke, D. Meso/Macroporous Silica from Miscanthus, Cereal Remnant Pellets, and Wheat Straw. *ACS Sustain. Chem. Eng.* **2015**, *3*, 2012–2021. [[CrossRef](#)]
25. Alyosef, H.A.; Ibrahim, S.; Welscher, J.; Inayat, A.; Eilert, A.; Denecke, R.; Schwieger, W.; Münster, T.; Kloess, G.; Einicke, W.-D.; et al. Effect of acid treatment on the chemical composition and the structure of Egyptian diatomite. *Int. J. Miner. Process.* **2014**, *132*, 17–25. [[CrossRef](#)]
26. Schneider, D.; Wassersleben, S.; Weiß, M.; Denecke, R.; Stark, A.; Enke, D. A Generalized Procedure for the Production of High-Grade, Porous Biogenic Silica. *Waste Biomass Valoriz.* **2018**, *11*, 1–15. [[CrossRef](#)]
27. Kumar, R.; Bhattacharjee, B. Porosity, pore size distribution and in situ strength of concrete. *Cem. Concr. Res.* **2003**, *33*, 155–164. [[CrossRef](#)]
28. Purnawira, B.; Purwaningsih, H.; Ervianto, Y.; Pratiwi, V.; Rochiem, R.; Purniawan, A. Synthesis and characterization of mesoporous silica nanoparticles (MSNp) MCM 41 from natural waste rice husk. *IOP Conf. Ser. Mater. Sci. Eng.* **2019**, *541*, 012018. [[CrossRef](#)]
29. Purwaningsih, H.; Ervianto, Y.; Pratiwi, V.M.; Susanti, D.; Purniawan, A. Effect of Cetyl Trimethyl Ammonium Bromide as Template of Mesoporous Silica MCM-41 from Rice Husk by Sol-Gel Method. *IOP Conf. Ser. Mater. Sci. Eng.* **2019**, *515*, 012051. [[CrossRef](#)]
30. Guo, Y.; Gou, K.; Yang, B.; Wang, Y.; Pu, X.; Li, S.; Li, H. Enlarged Pore Size Chiral Mesoporous Silica Nanoparticles Loaded Poorly Water-Soluble Drug Perform Superior Delivery Effect. *Molecules* **2019**, *24*, 3552. [[CrossRef](#)]
31. Imoisili, P.E.; Ukoba, K.O.; Jen, T.-C. Green technology extraction and characterisation of silica nanoparticles from palm kernel shell ash via sol-gel. *J. Mater. Sci. Technol.* **2020**, *9*, 307–313. [[CrossRef](#)]
32. Prempeh, C.O.; Formann, S.; Hartmann, I.; Nelles, M. An improved method for the production of biogenic silica from cornhusk using sol-gel polymeric route. *Biomass Convers. Biorefin.* **2022**, 1–11. [[CrossRef](#)]
33. Hassan, A.F.; Abdelghny, A.M.; Elhadidy, H.; Youssef, A.M. Synthesis and characterization of high surface area nanosilica from rice husk ash by surfactant-free sol-gel method. *J. Sol-Gel Sci. Technol.* **2013**, *69*, 465–472. [[CrossRef](#)]
34. Affandi, S.; Setyawan, H.; Winardi, S.; Purwanto, A.; Balgis, R. A facile method for production of high-purity silica xerogels from bagasse ash. *Adv. Powder Technol.* **2009**, *20*, 468–472. [[CrossRef](#)]
35. Norsuraya, S.; Fazlena, H.; Norhasyimi, R. Sugarcane Bagasse as a Renewable Source of Silica to Synthesize Santa Barbara Amorphous-15 (SBA-15). *Procedia Eng.* **2016**, *148*, 839–846. [[CrossRef](#)]
36. Setyawan, N.; Wulanawati, A. Simple extraction of silica nanoparticles from rice husk using technical grade solvent: Effect of volume and concentration. *IOP Conf. Ser. Earth Environ. Sci.* **2019**, *309*, 012032. [[CrossRef](#)]
37. Dhaneswara, D.; Fatriansyah, J.F.; Situmorang, F.W.; Haqoh, A.N. Synthesis of Amorphous Silica from Rice Husk Ash: Comparing HCl and CH₃COOH Acidification Methods and Various Alkaline Concentrations. *Int. J. Technol.* **2020**, *11*, 200–208. [[CrossRef](#)]
38. Sawasdeea, V.; Pisutpaisal, N. Rice Husk Ash Characterization and Utilization as a source of Silica Material. *Chem. Eng. Trans.* **2022**, *93*, 79–84. [[CrossRef](#)]
39. Mor, S.; Manchanda, C.K.; Kansal, S.K.; Ravindra, K. Nanosilica extraction from processed agricultural residue using green technology. *J. Clean. Prod.* **2016**, *143*, 1284–1290. [[CrossRef](#)]

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