

# The Extraction of Organic Silica from Agricultural Waste: A Mini Review

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## Abstract

Inorganic silica precursors, also known as alkoxysilanes, have been used commercially in many applications and synthetizations. However, it has been reported that these inorganic silicas can harm human health, causing stomach, bladder, and kidney failure, as well as death in the case of an acute inhalation. Due to this reason, organic silica from agricultural waste such as coconut husks, corncobs, sugarcane bagasse, rice husks, and bamboo leaves is being reviewed as an alternative source to replace the risky inorganic silica. This work discussed the extraction method, silica percentage obtained, and applications involving the use of organic silica, demonstrating that green waste can replace inorganic silica and provide good value to society.

## 1. Introduction

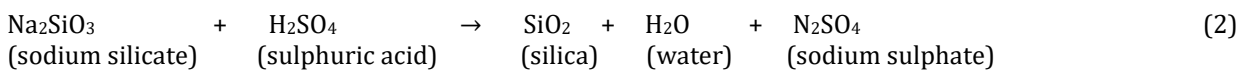
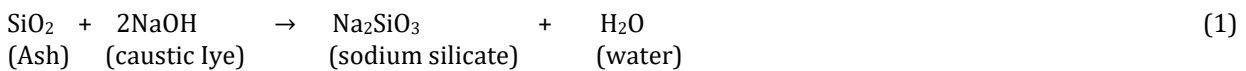
Solid waste produced by various industries like manufacturing waste, agriculture waste, and consumer waste is turning into a significant issue these days. In the Malaysian context, the massive amount of agricultural waste disposal is overwhelming, as the Malaysian economy has depended on agriculture for decades and has been the backbone of rustic improvement from that point forward. According to Mustafa and Ho in their research on agriculture wastes and the role of environmental law in Malaysia, despite the fact that Malaysia is becoming an industrial country, agriculture remains a major economic activity and will produce a lot of agricultural waste in the future since Malaysia is still geared towards the production of export commodities [1].

Before going into details about agriculture waste as an alternative to silica sources, various types of inorganic silica precursors, which are a subgroup of chemicals that are commonly referred to as alkoxysilanes, have been used commercially, such as TEOS, TMOS, THEOS, TMVS, and SS [2]. However, as reported in previous studies, the use of inorganic silica precursors can pose a risk to human health. Nakashima *et al.* reported that acute inhalation of TEOS could cause death at a specific time [3]. Okumura *et al.* also stated that TEOS could have an effect on acute stomach, bladder, and renal failure [4]. Meanwhile, Kolesar *et al.* mention that TMOS is recognized to induce edema, conjunctival hyperemia, and epithelial desquamation of the cornea in humans following contact [5]. Due to the risk, the commercial silica precursor needs to be replaced with a silica precursor that is better for the environment, safer, and cheaper. Organic silica obtained from agricultural wastes is said to be an alternative source to replace the risky inorganic silica precursor. Coconut husk, corncob, sugarcane bagasse, rice husk, and

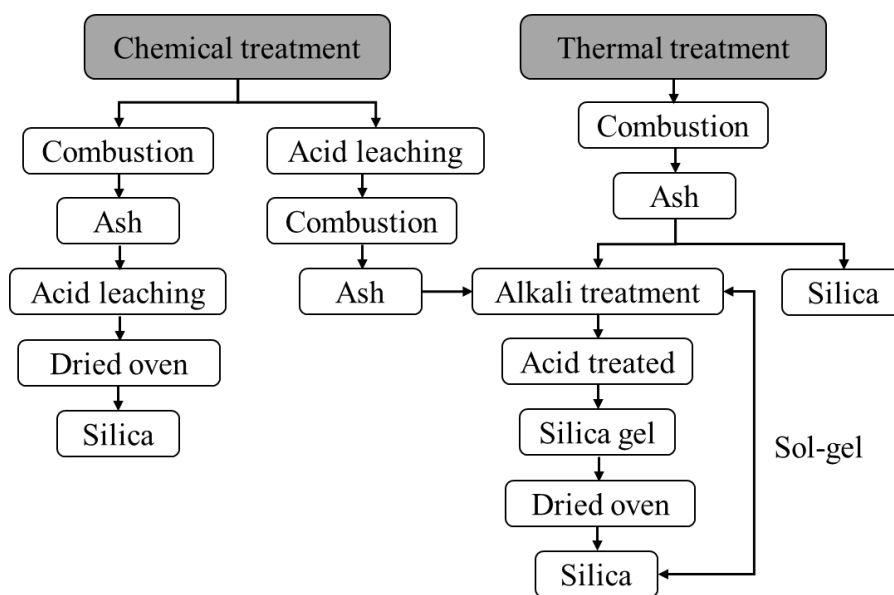
dry bamboo leaves are the agriculture wastes that attract the most interest from researchers due to the higher content of silica that can be obtained and used as an alternative precursor.

## 2. Extraction of Organic Silica

Previous studies have been intensively discuss on the methods of obtaining silica from agricultural wastes, such as sol-gel, precipitation, ionic liquid, microwave, thermal, and chemical treatment [6]. However, only three methods are commonly used, which are sol-gel, thermal, and chemical treatment methods. For the sol-gel method, silica ash was synthesized through simultaneous condensation and hydrolysis reactions where a sol of silicon alkoxide, or sodium silicate (SS), is converted into a polymeric network of gel. This synthesis procedure usually leads to silica precipitation under certain conditions, like restrictions on gel growth that involve coagulation and precipitation steps during its preparation. Silica gel prepared using this method can also be called xerogel. An example of the reaction from ash to silica gel begins with the reaction of ash with caustic lye (sodium hydroxide) to generate SS. After that, the SS will react with acids like HCl or sulphuric acid to obtain silica before drying to eliminate water and sodium sulphate [2]. The chemical reaction is as follows:



Meanwhile, two conventional and simple methods for extracting silica from agricultural wastes are chemical and thermal treatment methods. According to previous literature, the first step in gaining silica extract is by applying the chemical treatment before incineration, which is one of the most common technique. This process usually aims to remove impurities and some unwanted elements in agricultural wastes that can affect the outcome element of the organic silica. The usual treatment processes are washing and leaching via different acids such as HCl, sulphuric acid ( $\text{H}_2\text{SO}_4$ ), and nitric acid ( $\text{HNO}_3$ ). Between these acids, nitric acid is preferred due to its effectiveness in dissolving silica, impurities reduction, safety, handling, availability and affordability. Meanwhile, the different combustion temperatures for thermal treatment play a significant role in influencing the structure and properties of the extracted organic silica [7]. A general flow diagram for the extraction of silica by chemical, thermal, and sol-gel methods is shown in Fig. 1.



**Fig. 1** Flow diagram for silica extraction via sol-gel, chemical, or thermal treatment methods

### 3. Types of Agriculture Waste for Organic Silica Production

Generally, agriculture waste is known as one of the industries that generates abundant wastes such as corncob, sugarcane bagasse, coconut husk, rice husk, and bamboo leaves, as shown in Fig. 2 [8]. The disposal of this massive amount of produced waste is overwhelming since this waste could affect the world's environment. Due to this issue, much research has been done to use this waste and change it into a sustainable and profitable product. Agriculture waste is known as the cheapest source for silica production. Other reasons to consider agriculture waste as a good silica source, especially for large-scale production, are: (1) low-cost material; (2) containing high silica content; (3) comparable silica quality; (4) high energy content; and (5) fine-sized amorphous material [9]. It was also reported that agricultural waste could be potentially used as a source of silica for various applications. SiO<sub>2</sub>, or silica, is depicted as a valuable inorganic multipurpose chemical compound that emerges naturally as quartz, sand, soil, or flint and can be produced in many shapes, like gel, amorphous, and crystalline form [10]. Silica has also been broadly utilized in the industry as an additive in composites, catalysts, thermal insulators, drug delivery, electronic components, and ceramic engineering [11]. Thus, this utilization of silica from agricultural waste can boost industrial applications and help the sector raise income by using waste as a resource in its products.



Fig. 2 Various agricultural wastes as a silica source

Coconut is well known for its multiple functions and is often used in traditional ways, such as in food and cosmetic products [12]. With a large portion (35%) of the coconut husk, it is believed that coconut has good potential as an alternative organic silica source. Anuar *et al.* reported that the coconut husk produced up to 90% of the silica content in a crystalline form after going through chemical treatment [12]. On the other hand, Kurniawan *et al.* were able to get as much as 63.31% silica from coconut husk by thermal treatment. With the high content of silica that can be obtained, the utilization of coconut husk has proved to be economically viable as a silica source [13].

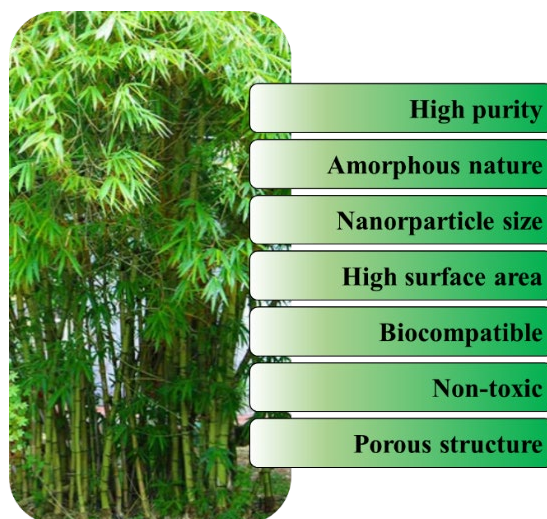
For corncobs, the cobs obtained from corn are primarily used as manure for agricultural production. Corncob is usually thrown out as waste or burned, which eventually causes an environmental impact. To avoid such a problem, many researchers have been working on using corncobs as an alternative silica source. For example, Mohanraj *et al.* in their study on the preparation and characterization of silica from corncob, recorded that thermal treatment followed by the sol-gel process managed to gain as much as 88% of silica content before undergoing the precipitation method to obtain nanosilica [14]. Okoronkwo *et al.*, produced silica xerogel by dissolving corncob ash with an alkali solution to form a sodium silicate solution, and the pH was adjusted using HCl to form aquagel. The silica yield from corncob ash was 52.32% with a moisture content of 2.89% [15]. Wardhani *et al.* investigated the production of silica from corncob using non-thermal and thermal methods. The highest silica content was observed after both acid treatment and combustion at high temperatures, with a 79.95% silica content [16]. Based on these reports, corncobs also have the potential to be an alternative silica source in the coming future.

Sugarcane is known as one of the most abundant crops in the world, with the cane representing 80% of the sugar produced. Sugarcane bagasse is an alternative waste product produced in the sugar industry after the extraction of sugarcane juice. The larger volume of bagasse produced has become a problem, and the importance of eliminating the material is compulsory. Chemical experiments have demonstrated that the ash obtained by burning the bagasse is rich in silica content [17]. Alves *et al.* achieved 99% silica purity, confirmed by X-ray fluorescence spectroscopy (XRF) by using alkaline extraction followed by acid precipitation [18]. Meanwhile, Natarajan *et al.* applied different heating temperatures of 500 °C and 750 °C to bagasse after acid treatment and compared it with the raw sample. The results indicated that 88% and 94% of silica purity were obtained for 500°C and 750°C, respectively, while 54% for the raw sample [19]. From the work, all the results obtained can be used as value-added for bagasse ash utilization and minimize the environmental impact of the disposal problem.

Rice husk is an abundant agricultural waste in many agro-based countries. The rice grain consists of 20% rice husk. Like bagasse, rice husk constitutes waste in rice-producing areas. Traditionally, rice husk has been burned or disposed of in landfills, but environmental regulation has limited this system. Due to that problem,

many researchers used and characterized rice husk by its negligible nutrition value and high ash content. Rice husk contains a high silica content as well as potassium, sodium, magnesium, calcium, iron, and smaller quantities of other components [20]. Madrid *et al.* processed silica from rice husk by washing, acid leaching, and calcination. Chemical treatment has enabled higher elemental removal efficiency, with at least 90% of the initial content of contaminants such as potassium and iron reduced [21]. Zulficar *et al.* produced tunable-size and high-purity silica using the sol-gel method. The extracted silica achieved 90.5% purity along with other impurities like  $\text{Al}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{MgO}$ , and  $\text{CaO}$  [22]. In their recent study, Azat *et al.* developed a new synthesis process for the production of high-purity silica. Mineral acid pre-treatment was changed to organic acid pre-treatment, which helps cut down on the number of chemicals used in silica extraction and treatment. The produced silica using a more environmentally friendly method had a high purity level of 98.67% and a surface area of up to  $625 \text{ m}^2/\text{g}$  [23].

Meanwhile, along with tengkawang, gondorukem, and rattan, bamboo is a member of the family Graminae and is a non-wood forest product. The most common part of bamboo used by the community is their rod, which is used in making papers, handicrafts, and medicines [24]. Other parts of the plant, such as roots, branches, and leaves, have not been fully utilized. Dry bamboo leaves were considered waste by the public, and it is regrettable since bamboo leaves are known to have a high silica content with an amorphous nature and nanoparticle size. Bamboo leaves are reported to have a high silica content of 17-23% by weight, which is higher than in rice husk (9.3-13.5%). Fig. 3 shows the notable properties of silica extracted from bamboo leaves. From previous study, Irzaman *et al.* created and tested two silica extraction methods: combustion to washing (silica A) and washing to combustion (silica B). The purity for each silica was 99.9% with the tetragonal crystal structure, and Mg, Au, and K impurities were found in silica A and not in silica B [25]. Silviana and Bayu synthesize nanosilica from bamboo leaves through magnesiothermic reduction after silica extraction using the sol-gel method. Silica and silicon content were determined using XRF and had a 96.3 wt% yield of extraction from bamboo leaves, while silicon yield was obtained at 61.2 wt% [26]. From the experiments, it was possible to utilize bamboo more optimally by extracting the silica content from the bamboo for various applications and fields. A summary of all agriculture waste used for the production of silica is shown in Table 1.



**Fig. 3** Properties of silica extracted from bamboo leaves [27]

Based on years of work, rice husk has been widely used in silica production compared to other agricultural waste. Starting in 2017, bamboo leaves have taken the place of rice husk since the abundant leaves can be collected anywhere as the plant itself is grown in various places such as the forest, farms for industrial purposes, as well as decorative plants. Bamboo leaves that fall to the ground are considered waste and always burned by the community, thus making it very regrettable since the bamboo leaves contain usable silica compounds [28]. In general, all bamboo parts have cellulose levels ranging from 42.4% to 53.6%, hemicellulose (cellulose and hemicellulose) levels ranging from 73.32% to 83.80%, lignin levels ranging from 19.8% to 26.6%, powdered and ash levels ranging from 1.24% to 3.77%, extractive levels ranging from 0.9% to 6.69%, and silica levels ranging from 0.10% to 1.28% [25]. However, the leaves are reported to have the most silica content. Bamboo leaf ash can produce almost 75% to 83% of the silica content [29]. Using various extraction methods, the silica content from bamboo leaves can be obtained for further use, such as being incorporated with other compounds to improve their characteristics and properties, thus replacing the use of synthetic silica that is harmful to human health.



#### 4. Conclusions

As the scope of agricultural waste is kept endless for years, there is an endless list of works involving silica extraction. The example of green materials that can be extracted for silica production might possibly increase since the society keeps producing waste in many aspects of real life. This review attempted to summarize all the work that has been done so far involving the extraction of silica from agricultural waste by citing all the examples from other works. Hopefully, this review is useful in providing knowledge about related work that can be used for further research works

**Table 1** Summary of silica extracted from agricultural waste

Agro-waste	Extraction	Results	Application	Ref
Coconut Husk	Thermal treatment	Silica obtained as much as 63.31%	Cement substitute	[13]
	Chemical treatment	Silica content increased to 90% after chemical treatment	Sample characterization	[30]
	Chemical treatment	90% of silica was extracted	Optical field	[31]
Corncob	Precipitation	88% of silica was extracted in a 3N NaOH solution	Sample characterization	[14]
	Sol-gel	Silica yield was 52.32% with a moisture content of 2.89%	Sample characterization	[15]
	Sol-gel	97.94% silica was obtained	Sample characterization	[32]
	Sol-gel	Silica content increased to 98.77% by sol-gel	Sample characterization	[33]
	Chemical treatment	Silica extracted using HCl produced the highest content of 79.95%	Sample characterization	[16]
	Sol-gel	-	Lead ions removal	[34]
	Thermal treatment	Silica obtained as much as 61.8%	Cement additive	[35]
Sugarcane Bagasse	Gasification & thermal treatment	28.39% by gasification and 31.82% to 34.26% by thermal treatment	Extraction comparison	[36]
	Chemical treatment	91.57% silica was obtained	Sample characterization	[17]
	Thermal treatment	76.168% for 500°C, 76.292% for 600°C, 77.286% for 700°C silica extracted	Combustion comparison	[37]
	Chemical treatment	Silica extracted using acid produced the highest content of 88.13%	Precursor to SBA-15	[38]
	Chemical treatment	Silica content increased to 90.6%-97% after chemical treatment	Reinforcing filler	[39]
	Sol-gel and precipitation	The purity of the prepared silica was 99%	Sample characterization	[18]
	Chemical treatment and sol-gel	Silica content was 88.68% and 99.08% for sugarcane waste ash and SiO <sub>2</sub> nanoparticles, respectively	Synthesis characterization	[40]
	Chemical treatment and sol-gel	Silica yields as high as 45.5% were achieved at a 2 mol/L NaOH solution at 90 min	Adsorbent for ethanol purification	[41]
	Sol-gel	Silica with acid treatment (SBA-500°C = 88%; SBA-750°C = 94%) is higher compared to raw SBA (54%).	Surface functionalizing agent	[19]
	Sol-gel	Freeze- and heat-drying silica during the sol-gel process is able to obtain above 98% silica content compared to raw ash (64.8%)	Filler for natural rubber composite	[42]
Thermal treatment	Silica obtained as much as 75.9% with other impurities	Pozzolan in concrete	[43]	
Chemical treatment	-	Water purification	[44]	

	Chemical treatment	For route A, sugarcane bagasse (43.6%-52.1%) and sugarcane leaves (59.3%-61.3%). For route B, both samples obtained around 50% silica, and for route C, 95.3% and 87.6%, respectively	Sample characterization	[45]
	Sol-gel and chemical treatment	Both ashes were produced above 95% purity of silica using sol-gel and chemical treatment	Sample characterization	[46]
	Chemical treatment	Silica obtained as much as 98.4%	Support for silver metal	[47]
Rice straw	Sol-gel	Highly pure amorphous silica was derived from the resultant rice straw ash by sol-gel at a 90.8% yield	Sample characterization	[48]
	Sol-gel	The heated rice straw contained 85% silica	Sample characterization	[49]
	Chemical treatment	Silica is extracted in cristobalite form with 91.46% crystallinity	Synthesis characterization	[50]
	Sol-gel	Silicon obtained as much as 17.45 at.%	Adsorbent	[51]
Rice husk	Sol-gel	Silica ash obtained as much as 91.40% with other impurities	Sample characterization	[52]
	Chemical treatment	Acid leaching allowed the removal of more than 90% of other metals to produce better silica purity	Sample characterization	[21]
	Sol-gel	Silica obtained as much as 99.08% after treatment	Sample characterization	[53]
	Chemical treatment	All silica obtained via different synthesis method is in the range of 85% to 95.4% purity	Hydrogen production	[54]
	Sol-gel	More than 90% of SiO <sub>2</sub> is recovered	Synthesis comparison	[55]
	Thermal treatment	Synthetic silica produced 99.6% of purity, followed by 1100°C and 700°C with 82.30 and 86.30% of purity, respectively	Sample characterization	[56]
	Thermal treatment and sol-gel	Nanosized, highly pure silica was produced in 99.9% amorphous form	Sample characterization	[57]
	Chemical treatment	Un-leached silica obtained 95.77% purity, and acid leaching produced more than 99% purity	Sample characterization	[20]
	Thermal treatment and chemical treatment	Both chemical treatments using acid and alkaline produced silica above 99% purity	Sample characterization	[58]
	Thermal treatment	Rice husk ash heated at 800°C for 2 hours is rich in amorphous silica content (91.74%)	Synthesis comparison	[59]
	Chemical treatment	Silica content was observed to be 89.85% using EDX	Sample characterization	[60]
	Chemical treatment	The average purity of the produced silica obtained using different synthesis methods ranged from 84.41% to 99.66%	Sample characterization	[23]
Dry bamboo leaves	Sol-gel	The silica content is high yield purity (99%)	Biomedical	[27]
	Thermal treatment and chemical treatment	Atom purity was 99%	Sample characterization	[25]
	Sol-gel	Silica obtained as much as 58.3%	Sample characterization	[28]
	Sol-gel	The silica product has a 96.3% yield of extraction	Li-ion battery anode	[26]
	Chemical treatment	The purity of silica for three different temperature rates is 65.85%, 74.49%, and 72.69%	Sample characterization	[61]

Sol-gel	More than 90% of silica was obtained together with minor impurities	Photocatalytic performance merging with TiO <sub>2</sub>	[62]
Sol-gel	-	Removal of methyl orange	[63]
Sol-gel	Silica content was obtained at as much as 85.57%	Removal of phenol	[64]
Sol-gel	Almost 99.9% of silica was extracted	Rhodamine B photodegradation	[65]
Thermal treatment	The relative abundance of silica was achieved at 52.29%	Cement	[66]
Sol-gel	-	Ceramics	[29]
Sol-gel	-	Membrane	[67]
Thermal treatment	Silica yield based on ash weight: 79.93%	Sample characterization	[68]
Chemical treatment	The composition of silica from bamboo leaves is 62.1%	Ceramic body glazing	[69]
Sol-gel	81.76% of silica was obtained	Synthesis of T-type zeolite	[70]

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## Conflict of Interest

Authors declare that there is no conflict of interests regarding the publication of the paper.

## Author Contribution

The authors confirm contribution to the paper as follows: **study conception and design:** Faiz Hafeez Azhar; **data collection:** Faiz Hafeez Azhar; **analysis and interpretation of results:** Faiz Hafeez Azhar, Zawati Harun, Rosniza Hussin, Siti Aida Ibrahim; **draft manuscript preparation:** Faiz Hafeez Azhar, Norsuhailizah Sazali, Siti Khadijah Hubadillah. All authors reviewed the results and approved the final version of the manuscript.

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