Review Article

An Overview of Current and Prognostic Trends on Synthesis, Characterization, and Applications of Biobased Silica

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Silica has shown numerous applications in different fields such as environmental, biomedical, agriculture, and even in chemical processing. However, due to high energy-intensive and cost-effective issues, researchers show interest to replace the conventional methods with biobased environmentally-friendly techniques for biosilica production from renewable biomass sources. Generally, silica is found to be available in amorphous and crystalline structures. For commercial purposes, silica is produced from alkyl orthosilicates ore that consists of polyethlydiorthosilicate, tetraethyl ortothosilicate, and tetramethyl orthosilicate. Another form of silica, silica gel, is produced from the selected resources of biomass, such as palm tree, wheat straw, maize leaves, teff straw, sugarcane bagasse, rice husk, rice straw, sugarcane leaf, oat husk, bamboo leaf, and corn cob. The production of biobased silica gel from agricultural residues is found to be a sustainable which receives a significant attention that can be replaced with inorganic-based silica gel for environmental concerns. Based on this context, there is a huge look for developing a process to produce biobased silica and silica gel from biomass resources with low energy utilization as promising alternatives to conventional methods. Keeping in view, current trends and methods for synthesis, the characterization of biobased silica and silica gel, as well as its wide prognostic applications were focused on a comprehensive review.

1. Introduction

Silica is a well-known material that is the most useful inorganic chemical compound for different industrial applications, such as environmental, biomedical, agriculture, and even in chemical processing. Commonly, it is found on the earth's crust and arises naturally as flint, sand, or quartz [1, 2]. Based on its structural characterization, silica gel has been found to be either amorphous or crystalline in appearance, which is observed as an inflexible 3-dimensional network of colloidal [3]. According to Kalapathy et al. [4], the structural character of the silica gel depends on its preparation method. Accordingly, it can also be categorized in aqua gel form, where the openings are occupied with water molecules in the xerogel aqueous phase, the openings are detached due to evaporation; besides, in the aerogel

form, the solvent portion is detached by supercritical carbon dioxide. Biomass can be a potential source for the extraction of synthetic silica components such as silica gel. In such a way, biomass resources ash of rice husk [5], sorghum bagasse [6], teff straw [7], maize leaves [8], rice straw [9], wheat straw [10], sugarcane bagasse [11], sugarcane leaf [12], bamboo leaf [13] corn cob [14], and palm [1] are found to be potential feedstock. Sodium silicate is used in general to extract the silica from the residual ash of the feedstock [15]. Further, the produced silica is treated with different types of acid such as sulphuric acid [16], hydrochloric acid [17], nitric acid [18], and acetic acid [19] to turn it into gel. Several investigations have proven that the silica particles have numerous industrial applications, such as the synthesis of shear thickening fluid, as adsorbents, and inert material, even as potential catalyst [20–22]. Bageru and Srivastava [7]

and Mizer [5] have documented that the silica gel materials have a strong adsorption capacity due to its high surface area $(700–800 \, m^2/g)$ with appreciable other physical properties. In specific, it exits excellent adsorption capacity on different organic compounds [23, 24]. The soluble forms of silicates derived from silica have remarkable industrial applications, especially, in pharmaceuticals and construction areas. The most common applications of liquid silicates are found in the development of ceramics [25, 26], concrete materials [27], glasses manufacturing [28], cement [29], delivery of biologically active ions [30], supercapacitors manufacturing [31], batteries [32], pharmaceuticals and cosmetics [33], detergents and adhesive agents [3, 4, 34]. Solid-state silica is used for various applications in the manufacturing of petroleum-derived products [35], fine-chemicals [36], bio-fuels [37], oil recovery [38], pollution abatement technologies and optical materials [4, 39], catalyst support [40], microfilters [41], thermal superinsulation [42], controlled release of drugs [23], and drug delivery systems for anti-biotics [34, 43].

Silica particles have also been demonstrated for their outstanding performance in influencing plant metabolic activities [44]; it helps as a fertilizer to improve seedling growth rate, root development, and increase water retention [45] in plants. Moreover, silica gel exhibits several applications as adsorbent in chromatographic separation and removal of organic pollutants in water purification systems [46].

Commercially, silica can be produced from alkyl ortho-silicates ore using the appropriate catalysts, such as poly-ethlydiorthosilicate, tetraethyl ortothosilicate, and tetramethyl orthosilicate [7]. Silica gel is prepared by acid precipitation method using sodium silicate solution, quartz, and soda ash at the elevated temperature. So far, the conventional methods, namely, precipitation [47], electrocoagulation [48], alkaline fusion [49], chemical vapor deposition [50], sol-gel [3, 51], fluidized bed technology [52], and hydrothermal methods [3] are employed traditionally for the production of silica gel. However, high-temperature calcination that reaches up to 1710°C is found to be one of the major drawbacks for silica gel production in the traditional existing methods [3, 49]. High-temperature reaction leads to energy-intensive process that has an adverse effect on developing an economically sustainable process for silica gel production and its marketing as well [10]. The conventional methods of producing silica gel limit its use in situations where product purity is not compromised because they contain contaminants such as heavy metals [6]. In addition, large-scale production of crystalline silica nanoparticles may release toxic matters into the working environment that may create unsafe working condition which causes occupational diseases, such as lung cancer and pulmonary tuberculosis [53].

Silica gel can be produced from renewable sources of selected biomass such as palm tree [1], wheat straw [10], maize leaves [8], teff straw [7], sugarcane bagasse [11], rice husk and rice straw [5, 9], sugarcane leaf [12], oat husk [54], bamboo leaf [13], and corn cob [14]. At present, agricultural residues receive significant attention as feedstock to produce silica gel due to sustainability, economic and environmental concern. However, developing a process for silica gel production with low energy and cost requirements using agricultural biomass material is still challenging [5, 7]. So far, different approaches for preparing silica gel from agricultural residues have been carried out, such as hydrothermal technique, chemical vapor deposition, combustion synthesis, sol-gel processing [7, 55, 56], and precipitation methods [39]. Upon the potential importance of silica and silica gel, this comprehensive review has been narrated to provide the different techniques used for the synthesis and characterization of biobased silica and its current and prognostic applications.

2. Biosilica

Silicon compounds are transferred from the roots to the shoots and deposited as the amorphous material SiO_2. Silica accumulations in the shoots of many plant species range from 0.1 to 10% [57]. Phytoliths are an accumulation of silicon in plants (amorphous hydrated silica) [58]. Usually, the concentration of stationary silicon compound is higher in older plant tissues, and the rate of build-up varies depending on the tissue. According to silicon accumulators makeup 7 out of 10 largely harvested crops. When compared with other natural systems, some crops have high silicon accumulation such as rice, sugarcane, and wheat that have ability to transfer more silicon from the soil. Therefore, plants, particularly crop wastes accumulate a lot of silicon, which might be thought of as an excellent source of biosilica [59]. Silica, produced from plant origins [60] has been identified to have better advantages compared to the silica obtained from synthetic or mineral sources. Such biobased silica can be synthesized using processes with less energy consumption, relatively simple, and environmentally friendly that do not require sophisticated infrastructure and costly reagents. The biobased silica powder obtained from plant sources comprises a slight amount of metal oxides which are considered impurities. However, the high purity silica at an affordable cost is an obligatory requirement. It has been clear that most waste by-products found from biomass residues create environmental concerns [5] such as attraction of pest and odor generation that might cause adverse effects on human health [61].

The studies conducted elsewhere revealed that the silica deposition in agricultural residues is significantly influenced by the availability and quantity of silicon present in the soil. The plant root system absorbs silicic acid from the soil and deposits it in the plant in the form of amorphous silica. Through the biological nature of the transpiration, silica deposition in the plant increase in all parts of the plants. Research outputs indicated that more water absorption could improve more silica deposition in the various plant components [20, 62, 63]. Currie and Perry [64] have reported that different plants were identified as significant contents of silica, such as wheat, rice, bamboo, sunflower, sorghum, and corn. Usually, silica has been deposited at leaves, stems, and other plants parts ranging from 0.1 to 10 w/w%. According to Currie and Perry [64] and Norsuraya et al. [61], present of silica content in agricultural residue can be varied with respect to species, season, plant maturity, and geographical location of the farm.

Table 1 presents the availability of silica composition in different agricultural residues reported by different investigators. From these observations, the presence of silica in various agriculture residues that vary from 46 to 95.5%; however, the composition depends on the type of biomass sources.

2.1. Biomass Source

2.1.1. Rice Husk and Straw. Rice husk has been investigated for its potential as an energy source as well as a source of silica [65]. Gu et al. [66] investigated in their research that rice husk ash is primarily made up of silica, which can be used in wastewater treatment and other industrial uses. Silica particle extraction from rice straw ash is a green approach that protects human health and the environment. The widely used process for producing silica in industries involves fusing sodium carbonate and quartz at high temperatures that range from 1700 to 2000°C for sodium silicate production, which is then precipitated with sulphuric acid to recover silica. Ma et al. [67] reported that 0.23 tons of carbon dioxide are released to the environment for every ton of silica produced, escalating the greenhouse impact. According to Carmona et al. [68] that rice husk contains around 20% minerals as well as organic compounds including cellulose, hemicellulose, and lignin, where silica makes up 94% of minerals, with the remaining 6% made up of aluminium oxide, potassium oxide, magnesium oxide, calcium oxide, and phosphorus oxide. The soil's composition varies from location to location depending on the kind of soil, fertilizers applied, and weather conditions [3]. Ramadhansyah et al. [69] observed that 93% of silica was gained from rice husk material. Moreover, from rice hulls contain 8.7–12.1% of silica content [70]. Trubetskaya et al. [71] report that the dry matter of rice husks contains a larger fraction of silica with 9.8%.

In yet another study, extracting high amount of silica using acid treatment method can be used to remove the presence of trace quantities of cations to increase the SiO_2 yield from the rice husk [70]. In such processes, the husk is subjected to calcination process followed by sodium hydroxide treatment in the preparation of sodium silicate. In order to control the size of nanoparticles, the aging time and temperature need to be adjusted during the reaction [72].

Rice straw differs from other cereal straws since it has high silica concentration and less lignin [73] and is referred to as a stem of plants [2]. In general, the stem is separated after harvesting rice grains and considered as by-product or biomass waste. It is found to be rich in silica. Different studies indicated that the silica content in the rice straw is comparatively higher than in other parts of the plants. Studies revealed that the composition of the rice straw ash content (13–20%), the percentages of cellulose (32–47%), hemicellulose (19–27%), lignin (5–24%), and other components (13–20%). Other ingredients in rice straw include silica, which makes up (60–80%) of the total weight. Owing to the silica content present in the ash obtained from rice straw, it can be considered a promising raw material for

silica synthesis [2, 9]. Khaleghian et al. [74] reported that the content of rice straw ash has 10–17%; from this, around 75% is the silica content. The chemical makeup of rice husk and straw has been reported by different investigators are summarized in Table 2.

Studies revealed that the rice husk from India and Cambodia have almost the same composition in the SiO_2 content (80% and 80.18%, respectively) [76, 77]. Besides, the rice husk from China had 94.79% of SiO_2 content [75]. In this line, the rice husk obtained from Bangladesh [79], Brazil, Canada, and Malaysia also have better silica content, such as 89.86%, 92.9%, 97%, and 93.1%, respectively [59]. It is apparent that based on its geographical nature, SiO_2 content in the rice husk is found to be low in Cambodian and Indian-based rice husk.

After rice husk, one of another important origins for silica are rice straws. Accordingly, rice straw from Indonesia (84.60%) [9] and Italy (83.20%) [77] were observed to similar in their silica composition. While comparing to the SiO_2 content of rice straw from the China (73.26%) [75], Egypt (57.90%) [78], and Vietnam (50.68%) [77], the yield of SiO_2 for Indonesian's and Italian's rice straw were found to be high. Yet another climatic factors, such as humidity level, air quality, sun light exposure, use of fertilizers, soil nature, and farming conditions, can also be decided the amount of silica present in the agriculture residues [78]. However, the husk obtained from the rice plant, contains 1.6 times more silica than the rice straw because of the plant's accumulation mechanism as aforementioned. Schneider et al. support this result and they observed that the rice husk has 1.8 times more silica content than rice straw [77] because of the biomass features where they are geographically located, even the other components contents also found to be varied.

2.1.2. Sorghum Bagasse. The grasses of sorghum can store silica in the form of silicic acid that can be precipitated as amorphous silica, commonly, known as phytoliths [81]. They absorb silicic acid from the soil and deposit as solid silica in their leaves. This mineral, which makes up 1–10% of the dry weight of grass mass, increases the resistance of plant to various stressors. However, even such a mineralization process is still poorly understood that needs to be investigated in detail about the mechanism for increasing stress tolerance [82]. Bioresidues from the red grain sorghum husk comprise both organic and inorganic materials, such as cellulose, hemicellulose, lignin, Na, Ca, Mg, Fe, K, Mn, Al, and SiO_2 [83]. With reacting low concentration hydrochloric acid to the sorghum husk particles at pressurized temperature followed by calcination, silica phytoliths could be extracted [84]. According to Periasamy et al. [85], significant amount of pure silica (95%) and negligible amount of magnesium were found in this biomass [85]. Sweet sorghum (*Sorghum bicolor* (L.) moench) is one of the common crops Africa sub-Saharan. It is a subsistence crop that can grow at different climatic environments. It is primarily utilized for the preparation of bioethanol [6], food, fuel, fiber, and brewing. The sweet sorghum bagasse is left as a solid residue that remains after collection of its grains. Its

TABLE 1: Percentage of silica in ash produced by different biomass sources.

Feedstock	Silica content (%)	Different methods	Calcination temperature (°C)	Type of materials	Structural properties	Reference
Rice husk	97.44	Sol gel	850@3 hr	Silica gel	Amorphous	[5]
Sorghum bagasse	96.36	Sol gel	600@3 hr	Silica gel	Amorphous	[6]
Teff straw	91.80	Hydrothermal	900@2 hr	Silica	Crystalline	[7]
Maize leaves	93.00	Leaching	500@4.5 hr	Silica gel	Amorphous	[8]
Rice straw	84.60	Extraction	500@2 hr	Silica	Crystalline	[9]
Wheat straw	83.00	Sol- gel	550@4 hr	Silica gel	Amorphous	[10]
Sugarcane bagasse	81.60	Sol gel	550@1 hr	Silica gel	Amorphous	[11]
Sugarcane leaf	80.14	Sol gel	600@1 hr	Silica gel	Amorphous	[12]
Bamboo leaf	75.90	Extraction	950@1 hr	Silica gel	Amorphous	[13]
Corn cob	52.32	Sol gel	650@3 hr	Silica gel	Amorphous	[14]
Palm	46%	Leaching	800@0.5 hr	Silica gel	Amorphous	[1]

bagasse has been mostly used to prepare the reinforcing composites woods, silage feed, and pulp manufacturing for paper. Studies on the composition analysis of sweet sorghum bagasse reveal that the contents vary with respect to its genotype, environment, and plant maturity [86]. Sorghum plant has eight different types, and all types show a significant variance in the amounts of ash, silica, iron, and calcium. In all the types, silica is found to be in the range from 8.10 to 10.78% in the ash obtained from its roots. The amount of ash in the sheath and leaves varied similarly. The roots' silica concentration ranged from 4.37 to 5.72% [87].

2.1.3. Teff Straw. Teff grain is a specific source of traditional food in Ethiopia. The chemical analysis on teff straw, which is grown on different parts of Ethiopia has been demonstrated with different compositions of silica. However, the chemical composition of teff obtained from various agro-ecologies was observed to be similar [88]. Commercially, Teff straw is worthless in Ethiopia except for traditionally used for animals feed and mud house construction as a binder. In some provinces, it has been under taken to open air burning to discharge the nutrients as manure for further cultivation. Nevertheless, this approach could cause air pollution on the surrounding [7]. More than two million tons of teff straw are thrown out with the trash each year. These are plenty enough for the production of silica material. Recently, different studies were documented on the teff straw utilization for the purpose of producing biogas, biomethane [89], and removing toxic heavy metal such as Cr (VI) from aqueous solutions [90]. According to [7], thermal method had been used to obtain 91.82% of pure biosilica from the teff straw.

2.1.4. Wheat Straw and Husk. Wheat is one of the most widely grown crops, covering more than 20% of the global agricultural product [91]. Wheat grain has better protein. It contains unique physical and chemical properties. It is consumed by major populations in the world because of its better protein content as compared to cereal crops, rice, and maize. It has very good source of carbohydrates and minerals such as phosphorous, potassium, calcium, magnesium, iron, boron, and zinc [92]. Wheat husk is a biomass residue remained after harvesting and mostly used for the

production of energy. Therefore, generating energy from wheat husk has great potential especially in the wheat producing countries. Wheat straw contains considerable amount of silica of about 9% that found in the form of hydrated which can be recovered as amorphous silica under a programmable burning condition [93].

In recent times, it is used as substrate for ethanol production in second generation process [94]. Waste biomass of the wheat straw is a promising renewable energy source in the forms of liquid, solid, and gas fuel. Additionally, when an agricultural by-product of wheat straw is burned, a significant content of SiO_2 can be obtained [95]. Besides, under a controlled burning condition, from the wheat straw can produced 10% ash, and from this ash can extract more than 70% of silica [96].

2.1.5. Bagasse and Leaves of Sugarcane. Sugar and ethanol are the most extensive commercial product prepared from sugarcane. A substantial amount of agricultural waste, such as straw and bagasse, are produced during the sugar-making process [11, 70]. Each ton of sugarcane is said to yield 200 kilograms of tips and straw and between 250 and 270 kg of bagasse, while processing the waste. The biomass created in the sugar manufacturing sector results in ash, which is either used as fertilizer or is just dumped in landfills. Therefore, the use of landfills causes some environmental and public health issues. Recently, construction industry led to employ the sugarcane waste ash instead of cement or sand. The sugarcane ash contains a substantial amount of silica. It could be a by-product with significant added value for different industries, such as tooth pastes and the rubber industry as strengthening agents [11].

The chemical makeup of different biomasses is shown in Table 3. According to these data, Wassie and Srivastava [99]; have reported that teff straw ash has a 52.23% silica [99]. However, Amibo et al. [98] observed the concentration of silica was observed to be 92.89% [98]. Ash from wheat husk comprised with 92.30% of silica [59]. From the studies documented by Alves et al., sugarcane bagasse has 72.74–81.60% of silica [11, 27]; besides, sugarcane leaf and wheat straw have showed, 80.14% and 73–73.15%, respectively. The level of the other inorganic by-products composition was found to be low.

TABLE 2: Composition of rice husk and rice straw ash by geographical location.

Chemical components	Composition in percent References												
	[75] China		[9] Indonesia	[76] India	Cambodia	[77] Italy	Vietnam	[78] Egypt	[79] Bangladesh	Brazil	[59] Canada	Malaysia	[76] India
	Rice straw	Rice husk	Rice straw	Rice husk	Rice husk	Rice straw	Rice straw	Rice straw	Rice husk	Rice husk	Rice husk		Rice husk
Silicon dioxide (SiO_2)	73.26	94.79	84.60	80	80.18	83.20	50.68	57.90	89.86	92.9	97	93.1	22.12
Aluminium oxide (Al_2O_3)	0.25	0.36	—	3.93	0.83	0.33	0.14	1.00	0.73	0.18	0.4	0.21	1.23
Ferric oxide (Fe_2O_3)	0.49	0.86	0.16	0.41	4.29	3.57	0.43	1.00	1.28	0.43	0.4	0.21	1.28
Calcium oxide	4.46	0.75	0.88	3.84	1.55	1.60	6.14	2.30	0.91	1.03	0.49	0.41	1.24
Magnesium oxide (MgO)	2.14	1.86	0.44	0.25	0.81	1.00	2.32	3.40	1.16	0.35	0.50	1.59	0.21
Sodium oxide (Na_2O)	0.93	0.39	—	0.67	—	—	—	—	—	0.02	1.12	—	—
Potassium oxide (K_2O)	13.46	1.86	6.39	1.45	3.89	2.73	21.11	14.60	—	0.72	3.0	2.31	—
Manganese oxide (MnO_2)	0.04	0.02	—	—	—	—	—	—	—	—	—	—	0.074
Phosphorus oxide (P_2O_5)	1.94	0.23	—	3.80	3.80	4.12	0.77	13.80	—	—	—	—	—
Sulfur trioxide (SO_3)	2.41	0.09	—	0.78	2.05	1.52	2.14	3.20	—	0.10	0.24	—	—
Titanium oxide (TiO_2)	0.05	0.02	—	—	—	—	—	—	—	—	—	—	—
Chlorine (Cl_2)	0.57	0.08	—	—	—	—	—	2.30	—	—	—	—	—
Other components	—	—	7.53	2.60	2.60	1.92	—	0.50	—	—	—	—	—
Loss on ignition [80]	—	—	—	8.56	—	—	—	—	4.26	—	—	—	73.87

TABLE 3: Composition of teff straw, wheat husk and straw, sugarcane bagasse, and leaf ash based on its geographical location.

Chemical components	[97]	[98]	[99]	[59]	Turkey	[100]	[59]	[11]	[12]
		Ethiopia		Bangladesh	Wheat husk	Pakistan	Bangladesh	Brazil	India
		Teff straw ash		Wheat straw		Wheat straw	Sugarcane bagasse	Sugarcane bagasse	Sugarcane leaf ash
Silicon dioxide (SiO_2)	91.81	92.89	52.23	73	92.30	73.15	72.74	81.60	80.14
Aluminium oxide (Al_2O_3)	0.42	<0.01	1.55	3.90	—	—	5.26	7.94	0.89
Ferric oxide (Fe_2O_3)	0.71	0.23	9.74	1.75	0.647	1.67	3.92	2.31	0.51
Calcium oxide (Zhang et al.)	3.43	1.67	17.66	8.12	4.17	5.78	7.99	0.98	6.06
Magnesium oxide (MgO)	0.81	0.82	1.97	2.80	—	1.78	2.78	1.26	5.02
Sodium oxide (Na_2O)	0.74	<0.01	—	—	—	—	0.84	0.26	0.28
Potassium oxide (K_2O)	0.29	0.19	3.92	—	2.60	3.87	3.47	2.10	3.09
Manganese oxide (MnO_2)	—	<0.01	2.39	—	0.12	—	—	0.06	0.17
Phosphorus oxide (P_2O_5)	0.95	0.29	3.92	—	—	—	—	1.07	—
Sulphur trioxide (SO_3)	0.63	—	4.11	—	—	—	—	0.52	2.25
Titanium oxide (TiO_2)	—	<0.01	0.69	—	0.074	0.96	—	0.67	0.046
Chromium oxide (Cr_2O_3)	—	—	0.82	—	0.052	—	—	—	0.0067
Coper oxide (CuO)	—	—	—	—	—	—	—	—	—
Water (H_2O)	—	1.34	—	—	—	—	—	—	—
Chlorine (Cl)	0.21	—	0.38	—	—	—	—	0.36	0.69
Other components	—	—	—	—	—	—	—	—	—
Loss on ignition [80]	—	2.45	—	—	0.037	2.38	—	0.79	—

2.1.6. Corn Cob. Corn or maize is one of the well-known crops, which is frequently utilized as food in the world [3]. The waste material from the corn is corn cob husks. In corn cobs, silica considers the main inorganic component [101, 102]. It is obtained in huge amount from the production of corn processing as a waste. Normally, the by-products, corn cob, are stored and burned in an open area. Corn cobs contain notable amount of amorphous silica [56, 103], which could be converted into silica after burning in air and followed extraction using alkaline or acid solutions [103]. According to [3], the ash generated from corn cob comprises around 60% of silica. They have used a well-grounded powder to produce silica, silica nanoparticles, and silicates [3]. On other hand, the silica in corn plants is found to be accumulated in other parts of plants such as fruits, leaves, stems, seeds, and roots [39].

2.1.7. Bamboo. Bamboo is very famous biomass made by lignocellulosic material. Using bamboo, different value-added goods are attained. It is known to be nonwoody plant commonly produced by primary shoot. It has various uses, starting from different domestic products up to industrial utilization, such as nutrition, paper, pulp (textile, toys, medicine sector, and aircrafts [104]), and building materials [70]. However, the leaves obtained from the bamboo plants are often considered as waste materials that receives comparatively less attention. Nevertheless, it has some significance in terms of presence of silica compounds, which can be extracted and utilized [13]. Studies report that the silica content of ash obtained from the bamboo leaf after washed using acid was found to be significant [70]. Hence, bamboo has similar chemical composition that of wood, however, in terms of minor components, bamboo is known to be higher content compared to wood [104].

Chemical composition analysis reveals that constituents of bamboo fiber primarily consist of hemicelluloses, cellulose, and lignin. This contributes around 90% of total biomass of the bamboo. It is also found that the presence of the minor components such as tannins, fat, protein, pigments, pectin, resins, inorganic salts, ash, and waxes in the bamboo biomass. These ingredients are the key responsible for the physiological activity of bamboo. Generally, they are found in cavity of cells or special organelles [70].

2.1.8. Palm Mill Fly Ash. Palm oil is very famous which is produced from palm (*Elaeis guineensis*) [105]. In the view of silica-containing agrowastes, fly ash obtained from palm oil mill can be a potential resource [54]. Around four million tons of wastes are produced from palm oil mill per year in Malaysia, which is the largest world producer. In the palm oil processing, mills are utilized only 10% of the palm fruit bunches, whereas the remaining 90% are simply discarded [106]. During the combustion of residues, palm-oil-fuel-ash is found to be a by-product from processing of palm oil [107]. The solid waste consists of 15% shell and 85% fiber that are utilized as boiler fuel whereas the 5% fuel might be leftward as unburned material that generates ash. Alkaline extraction and sol-gel precipitation using sulphuric acid have been extensively used to produce silica that can be precipitated from palm oil ash. However, the process with the use of sulphuric acid requires a large volume of chemicals which makes the processing cost expensive. Recently, by another way, CO_2 is employed to reduce the amount of chemicals needed for this process. In addition, this method can destabilize the silica extract easily for the recovery of sodium hydroxide [54].

Table 4 demonstrates the biomass chemical composition. Where bamboo leaf ash contains silica with a range from 75.90 to 82.86% [109, 111], followed by ash from corn cob from 27.80 to 66.38% [59, 108, 111], and palm ash 40.60–63.60% [1, 59, 110]. The other by-products from the inorganic composition were at a lower level compared with the major components.

Ashes from bamboo leaves, maize cobs, and palm leaves were analyzed, and it was discovered that they included oxides of aluminum, sodium, calcium, potassium, iron, zinc, magnesium, titanium, phosphorus, sulphur, and chlorine.

3. Synthesis of Biobased Silica from Biomass Resources

3.1. Preparation of Biosilica from Selected Biomasses. Silica is extracted from different biomass sources using different extraction methods. Silica is extracted from the rice husk by two methods, extraction with alkaline solution, and sol-gel technique [5]. These methods are found to be economically feasible for the silica production [4]. According to [10], wheat straw is treated with hydrochloric acid in microwave digester. After removing the excess acid, it was calcinated at 550°C. Then, the fine white powder was obtained. Teff straw is also one of the most important silicas bioresources, while silica is synthesized from teff straw using hydrothermal method by refluxing with HCl at 80°C for 1 h. The prepared silica can be subjected to characterize using different techniques to understand the physical and chemical properties [7, 11]. Recently, the use of corn cob for the biosilica production is significantly concerned by most of the studies. Initially, corn cob is subjected to grind to obtain fine powder using size reduction techniques. In another way, silica is obtained from the ash of corn cob using the acid precipitation method [3]. In elsewhere, maize leaves are used for silica production using leaching method [8]. Sugarcane bagasse and leaves are another bioresource for biosilica [3, 70]. Palm tree ash also has been investigated for silica production by treating with acids. For this, appropriate concentration of sulphuric acid, hydrochloric acid, and nitric acid solution were widely used for silica extraction [1].

During acid extraction, the biomass residue was washed and dried after that the size of the residue treated by HCl solution. Then it was dried in over with temperature of 60°C for 24 h. Followed by subjected to burn in a furnace for 6 h at 800°C.

3.2. Preparation of Biosilica Nanoparticles from Selected Biomasses. A beaker was contained 5, 10, and 15% of NaOH solution and combined with rice husk ash. The mixture was

TABLE 4: Composition of corn cob, bamboo leaf, and palm ash by geographical location.

Chemical components	Composition in percent							
	Reference							
	[59] Bangladesh	[14] Nigeria	[108] Indonesia	[109] India	[13] Indonesia	[59] Bangladesh	[1] Malaysia	[110] Malaysia
	Corn cob			Bamboo leaf	Bamboo leaf	Palm ash	Palm ash	Palm ash
Silicon dioxide (SiO_2)	66.38	47.78	27.80	82.86	75.90	63.6	45.50	40.60
Aluminium oxide (Al_2O_3)	7.48	9.40	5.70	1.14	4.13	1.6	5.40	3.71
Ferric oxide (Fe_2O_3)	4.44	8.31	4.69	0.32	1.22	1.4	3.26	15.74
Calcium oxide (Zhang et al.)	11.57	16.70	14.03	2.57	7.47	7.6	12.80	19.60
Magnesium oxide (MgO)	2.06	7.80	9.50	1.35	1.85	3.9	3.20	1.30
Sodium oxide (Na_2O)	0.41	1.89	—	0.18	0.21	0.1	—	—
Potassium oxide (K_2O)	4.92	5.42	18.49	3.27	5.62	6.9	23.30	13.80
Manganese oxide (Mn_2O_3)	—	2.70	—	—	—	—	—	0.28
Phosphorus oxide (P_2O_5)	—	—	—	—	—	—	5.38	2.73
Sulphur trioxide (SO_3)	—	—	—	—	1.06	—	—	0.44
Titanium oxide (TiO_2)	—	—	—	—	0.20	—	—	0.35
Other components	—	—	—	—	—	—	1.16	—

agitated for three hours. The residue is washed with distilled water after filtering the final mixture. The filtrate from this extraction is sodium silicate solution. The sodium silicate solution's starting pH was calculated. When a gel forms or condensation with an acid solution occurs, add HCl, and stir until pH 7 is reached. To describe the gel, it was filtered, rinsed with distilled water, and dried for three hours at 100°C [112]. In other investigations, wheat straw samples were burned off using a muffle furnace at 500°C for 8 hours before being subjected to reflux boiling in a 10 percent (v/v) aqueous solution of HNO_3. The samples were then completely cleaned with distilled water before being burned of 400, 500, 600, and 700°C, respectively. For this process porous silica nanoparticle was prepared [113].

3.3. Methods of Preparation.
Silica is prepared from different biomass resources [2] using various methods such as hydrothermal technique, combustion synthesis, chemical vapor deposition, microbial hydrolysis processing [7], sol-gel processing [10, 11], and chemical vapor deposition [114].

3.3.1. Sol-Gel Method.
Sol-gel is a process by which a transformation occurs in colloidal suspension of sol into gel through 3D interconnecting network. This process yields homogeneous and pure sol-gel. Sol-gel method can be further processed to get different forms of desired materials such as films, fibers, and powders in submicron forms [3]. In this method, suspension of concentrated hydroxide or metallic oxide (sol) is involved. The sol is dehydrated through evaporation which results in a semirigid mass, colloquially, and gel. In a controlled heating, the gelated material can produce pure and mixed oxides. The properties of a particular sol-gel network are related to different parameters, such as temperature, pH, reagent concentration, time of reaction, concentration of added catalyst, drying, and aging temperature. These factors are significantly affecting the condensation reactions and rate of hydrolysis [114]. The reaction is controlled by the reactants of alcohol, acid/base,

and water. The particle size can be adjusted by precursor concentration, pH, and reaction temperature [3]. In general, the sol-gel technique requires important steps in order to obtain final metal oxides which comprise condensation, hydrolysis, and rate of drying. Accordingly, the metal precursor is taken to rapid hydrolysis reaction to produce solution of metal hydroxide. In the process, a condensation process leads to result in a 3D gel. By the end of the process, the gel product is dried, and converted to a xerogel [115].

Sol - gel method is the most extensive method and applied to prepare silica gel. Table 1 summarizes amorphous silica and the yield of silica gel from various biomass. To eliminate the volatile material from the sample, rice husk ash was calcined at 700°C for five hours. To create sodium silicate solution, rice husk ash that had undergone thermal calcination was extensively combined with alkali solution. Through the neutralization of a sodium silicate solution, silica can be produced. According to Ananthi et al. [18], the rice husks can be steeped in nitric acid and precipitated silica to achieve the maximum amount of sodium silicate solution [18].

According to [61], the silica gel content was leached out from the aqueous phase in the form of soluble sodium silicate according to

$$SiO_2 (Ash) + 2NaOH \xrightarrow{\text{yields}} Na_2SiO_3 + H_2O \quad (1)$$
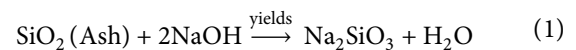
Then, silica gel was started to precipitate when the pH decreased to <10. The precipitation of silica gel has been carried out according to

$$Na_2SiO_3 + 2HCl \xrightarrow{\text{yields}} SiO_2 + 2NaCl + H_2O \quad (2)$$
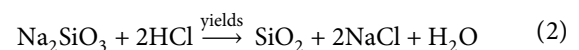
The solution (sol) was aged in mother solution at room temperature for 20 hr and called silica gel [4].

Sol-gel method is able to produce thin and thick coating. It has the capacity of sintering at low temperatures (200–600°C). Sol-gel method is efficient with economic feasibility that can produce better-quality product. However, this method has some drawbacks, such as the product

resulted with residual hydroxyl and/or carbon groups. It needs long processing time. The use of organic solutions may result in handling of toxic [116]. The process flow for creating silica gel from agricultural waste is shown in Figure 1.

3.3.2. Hydrothermal Method.

Hydrothermal process is a proven method for synthesis of nanomaterials. It is principally a solution reaction-based approach [117, 118]. This method generally carried out at elevated temperature and high pressure for crystal growth or crystal synthesis since the substances is insoluble in normal temperature of less than $100°C$ and pressure of less than one atmosphere. The elevated temperature of $250–300°C$ can produce the maximum ionic product. In most of the time, hydrothermal synthesis is carried out below the temperature of $300°C$. However, the temperature about $374°C$, and pressure, 22.1 MPa are found to be the critical condition. Studies showed that under supercritical condition, the dielectric constant, and solubility of compounds solvent properties can be changed dramatically.

Because water has a dielectric constant of 78 at ambient temperature, polar inorganic salts can be dissolved in it. The dielectric constant exhibits a decreasing trend while temperatures rise and an increasing trend while pressure falls. As a result, due to the enrichment of the reaction rate, and massive supersaturation produced by the theory of nucleation, supercritical water offers a potential reaction field for particle development, and lowering its solubility [119]. The hydrothermal process can produce crystalline segments that are unstable at their melting point. This process is suitable for growing crystals of excellent quality while maintaining good control over their alignment. Basically, the process via which metallic oxide units develops the process of creating metallic salt solutions, including hydrated metallic ions [119]. The hydrothermal process can produce crystalline segments that are unstable at their melting point. This process is suitable for growing crystals of excellent quality while maintaining good control over their alignment. Basically, there is the process via which metallic oxide units develops. It is used to create metallic salt solutions using hydrated metallic ions that hydrolyze to metal hydroxides and then continue to precipitate to metal oxides after dehydration. Hydrolysis is an electrostatic interaction between metallic ions and hydroxyl ions.

Hydrolysis method is proven to be more effective for determining the precise physical characteristics of novel compounds and multicomponent physicochemical systems under high pressure and temperature [114]. After acid refluxing, biomass material samples can be used to make biosilica components by hydrothermally decomposing the organic constituents in an electric muffle furnace. 50 grams of teff straw were placed in an electric muffle furnace and burned for two hours at different temperatures (500, 700, and $900°C$) to produce ash. This experiment was conducted by Bageru and Srivastava. They noticed that the teff straw ash products include substantial amounts of biosilica components [7]. The availability of agricultural waste products that can be converted into silica material is shown in Figure 2.

The yield of silica from various biomass is shown in Table 1 with the majority of this method's crystalline silica being created for further use.

3.3.3. Chemical Vapor Deposition Methods.

Commercial nanoparticle material synthesis frequently uses chemical vapor deposition (CVD). For a technique of components exposed to one or more volatile pioneers, CVD is employed. The pioneers breakdown or react on the surface of the substrate to produce a tinny film or nonvolatile firm sum. The majority of its applications involve coating faces with thin films. CVD is also utilized to produce highly pure nanocomponents, powders, and to build resource combinations using penetration methods [3].

The chemistry is ludicrous and many different kinds of chemical reactions are intertwined due to the multipurpose environment of CVD [120]. Single-walled carbon nanotubes (SWNTs) are produced generally at lower temperatures of $600–900°C$; however, higher temperatures of $900–1200°C$ reaction encourage the formation of SWNTs. On occasion, depending on the type of ingredients, carbon nanofibers and nanobeads are also produced. A recent study discovered that utilizing a superior nitrogen-pretreatment of the Fe-Mo/MgO reagent, thermal CVD could make SWNTs with substantially graphitized structure. Since it was concluded in the complete comment that nitrogen-pretreatment enhances catalytic activity and supports the development mechanism to manufacture elongated SWNTs, it is similarly formed, extremely graphitized SWNTs of enlarged size [114].

The method that has been used commercially to remove silica fine particles is one specific benefit of CVD [121]. However, the drawbacks of CVD include peculiar equipment and potentially hazardous gaseous unsatisfactory yields [3]. Another difficulty in the CVD manufacturing process is controlling the stage structure, particle diameter, and shape [114, 121]. Due to the gaseous undesirable products' high level of poisonousness, CVD requires specialized equipment.

This method of preparation involves depositing a thin layer of gaseous reactants on the substrate. By combining the gas molecules in a reaction chamber at room temperature, deposition is produced. A chemical reaction occurs when a heated substrate comes into contact with a gas mixture, and a thin film is produced on the surface. This thin layer can be kept and applied in numerous ways. The primary deciding factor in this method is the temperature of the substrate. This process produces evenly sized, exceptionally pure, and mechanically stable nanoparticles. Two drawbacks of CVD are the requirement for specialized equipment and the severe toxicity of the gaseous by-products [122].

3.3.4. Coprecipitation Method.

Complications may be situated where this type of method is infrequently agrees to attain worthy macroscopic homogeneousness [123]. Its production includes suspension of compounds of precursor salt in media of aqueous followed by pH arrangement the precipitate in the solution [114]. For metallic compounds of two or more alignment the solubility of the constituents
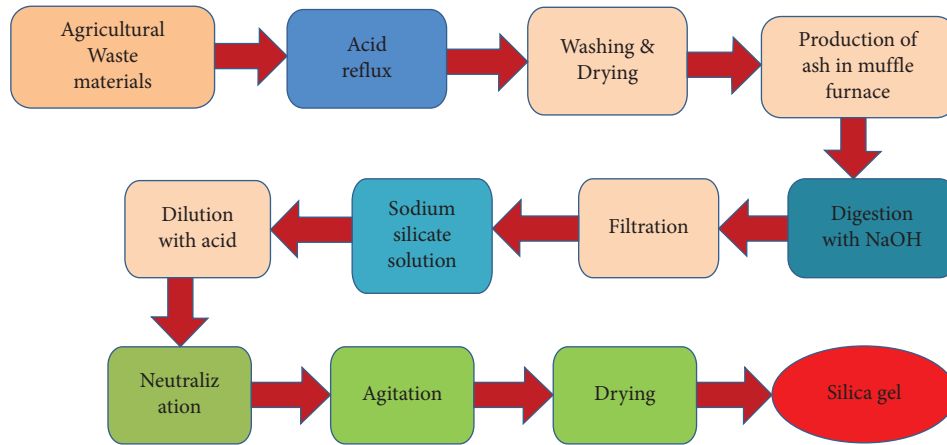
FIGURE 1: The process flow diagram for making silica gel from agricultural waste.
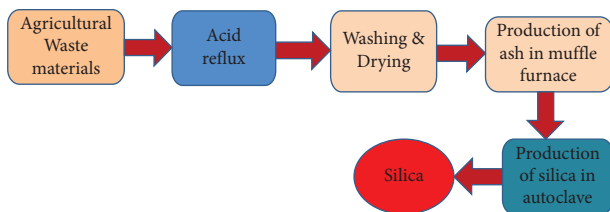

FIGURE 2: Schematic illustration of provision of agricultural waste materials converts into silica material.

FIGURE 3: Schematic illustration of the silica gel extraction process.

differs depending on the precipitate which occurred during precipitation. Normally, for a condition of poor mixing or a slow precipitate in the reaction intermediate, the precipitate which shows a heterogenous and coprecipitation method is preferable one compared with other techniques [123]. For preparation of metallic oxide powders and ceramics material this method is preferred. Coprecipitation techniques preferred not only as a simple method but also easy for mixing of metallic ingredients which produces with a low temperature treatment with perfect stoichiometry [114]. To prepare molecular sieve for converting amorphous to crystalline constituents with better thermal stability, using hydrothermal treatments is preferred [123] rather than this method. Silica gel acquired from different biomass materials are presented in Table 1. Figure 3 presents a schematic illustration for silica gel extraction process.

3.3.5. Leaching Method. Leaching is nothing but eliminating constituent from solid through liquid withdrawal media. In this method, the natural solid form the preferred constituent spreads into the solvent. Three imperative parameters are found to be most important in leaching process that are solvent selection, interaction time, and temperature. Temperature must be attained to optimize production of bulk transfer and solubility. It can be distributed into two classes, namely, dispersed solid, and percolation. However, solids are contacted with the selected solvent in the classes of percolation and broadly used for exciting the solid quantity. Whereas, for dispersed classes usually the solid becomes grounded into small before adding into the selected solvent.
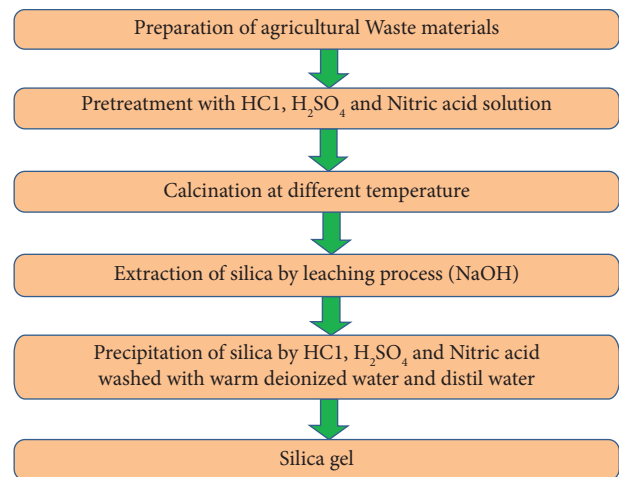
Additionally, liquid is added into the quantity of solid and vice versa for the case of dispersed classes. To prepare metallic oxides of silica, nitric, hydrochloric, and sulphuric acids are widely applied [1, 8].

Temperature of 90°C is better than 80°C for leaching performance of silica from rice husk ash which increased from 92.40% to 99.30%. Similarly based on this performance the Fe_2O_3 decreased from 2.26 to 0.43% at 90°C. With the elevated temperature, the acid molecules gotten an additional kinetic energy, because of this the molecular movement greatly increment, which results the rate of chelating increased. In addition to this, the smaller the particle size of the rice husk which gain larger surface area exposed and making easier mass and heat transfer to the prepared husk powder thus contributing in increasing leaching rate [124]. Temperature and particle size are the main determinant factor to enhance leaching process effect.

Sol-gel, chemical vapor deposition, hydrothermal, and leaching are a few of the various reported approaches that have been summarized. Comparing the sol-gel approach traditional methods, there are a number of benefits. Sol-gel techniques sometimes include trade-offs for better control of

surface area, pore volume, and size dispersion. Additionally, it is superior to other conventional methods for generating high-quality materials that are homogeneous and pure at low temperatures.

4. Characterization

Synthesized biobased silica material derived from the selected biomass resource is characterized using different techniques. The major characterization techniques include Brunauer–Emmett–Teller (BET), transmission electron microscopes (Rodella et al.), X-ray fluorescence, X-ray diffraction (XRD) method, thermo gravimetric analysis, differential thermal analysis, Fourier transforms infrared spectroscopy, Raman spectroscopy, and scanning electron microscopes [125].

4.1. Brunauer–Emmett–Teller (BET). Adsorption is the process by which gas molecules or atoms attach to a surface. The exposed surface area, temperature, gas pressure, and the degree of gas-solid interaction all have an impact on how much gas is adsorbed. Because it is readily available in high purity and interacts strongly with the majority of materials, nitrogen is often used in BET surface area analysis [126]. In the BET method, where P is the system pressure and P_0 is the initial pressure, the specific surface area can be evaluated in the relative pressure range (P/P_0) of 0.05 to 0.25. The silica nanoparticles' pore volume was calculated using a pore size analyser using the nitrogen adsorption isotherm at a relative pressure P/P_0 of 0.3 measurements of the porous size distribution [66]. The nitrogen adsorption isotherm of rice husk ash at 77K is with a plateau near the relative pressure ($P/P0$) of 1.0 was not reached by the adsorbed volume of nitrogen on rice husk ash [127].

In studies elsewhere, Prempeh et al. [128] determined the surface area using the BET equation for pressures between 0.05 and 0.3 (P/P_0) is fitted on the data of adsorption in BET analysis the adsorptive gas of nitrogen at 77K for this the molecular cross section of it works with standards value of 0.162 nm^2. At 0.98 the relative pressure of total volume was determined. Using an indirect molecular adsorption technique, characteristics of the pore size can be determined.

Particle size reduction often supports adsorption, a surface phenomenon. Smaller biomass particles are said to have a higher ability for adsorption than bigger ones. Since adsorption capacity and BET surface area are directly inversely related, larger particles with more BET surface area should result in better removal rates [136]. The surface area, pore volume, and pore size of various types of silica gel, silica, and biomass ash are shown in Table 5. The generated ash from bamboo leaves had a maximum specific surface area of 667.95 m^2/g, a total pore volume of 58.4 ml/g, and an average pore diameter of 99.97 nm after being heated to 600°C for 4.5 hours. [134] following that, rice husk ash was discovered to have an average pore diameter of 1.98 nm, total pore volumes of 0.6464 ml/g, and a specific surface area of 653 m^2/g [135]. Silica obtained from the rice straw ash with surface area of 413 m^2/g, total pore volumes of 0.2 ml/g

and 1.9 nm as the average diameter of the pore [133]. Similarly, the highest surface are of silica gel from teff straw with temperature 750°C at 2 h was found to be 305 m^2/g [98] afterward, sugarcane bagasse silica with a surface area of 265 m^2/g, total pore volumes of 0.425 ml/g, and an average pore diameter of 6.250 nm came in second [11].

4.2. X-Ray Diffraction (XRD). XRD method is known to be an effective technique which is used to determine the crystal structure of any materials [137, 138]. XRD analysis was conducted by comparing the diffraction lines of the samples with those in standard from the powder diffraction [125]. Based on this standard, XRD can determine the crystalline nature of particle of bigger size of 3–5 nm. The chemical phase configuration and the bulk materials of crystalline can be analyzed using XRD. XRD instrument have electromagnetic radiation which has a wave length size that ranges from 0.01 to 0.7 nm. This range is comparable with spacings of the lattice planes in crystalline form. The spacing size of metallic atoms always is between of 0.2-0.3 nm. X-ray photons are dispersed in a diverse way whereas the X-rays beam incident interrelates with the exact atom. When there is no change in incident photon and different photons of energy were scattered, and this revealed their elastic nature. The superposition of distributed waves and the advantageous behavior of wave phase interference are both possible. However, because of the phase, destructive interference cannot occur. The creation of periodic planes in coherent stutterers is caused by the atoms' crystalline planes. When different kinds of atomic planes are created by diffraction patterns, which provide information about how the atoms are arranged within crystals.

The amorphous nanosilica was discovered at the peak of 2 equal to 220 in the prepared rice husk ash at temperatures of 500, 700, and 1000°C. According to the silica activity index, the absence of the crystallin phase is largely supported by the lack of strong peaks that would have indicated the absorption of crystal structures that were organized. When rice husk is prepared sustainably at a lower temperature, potassium is found since there are no carbon peaks, and the material is porous. In contrast, the rice husk needs to be washed in acid solution prior to thermal treatment in order to primarily remove the potassium content and remove any fixed carbon from the raw materials. The particles' half-width of the peak can be calculated using (3) Scherer's formula.

Scherer's formula can be expressed as follows:

$$D = \frac{K * \lambda}{\beta * \text{Cos } \theta}, \tag{3}$$

where K (constant) $= 0.9$ nm, $\lambda = 1.542$ Å (angstrom) by means of wavelength Cu-Kα and radian of β. The nanosilica materials were produced near to 7 nm, these results can be determined manually using the chart of XRD [139]. According to Bageru and Srivastava [7], the amorphous nanosilica was discovered at the peak of 2 equal to 220 in the prepared rice husk ash at temperatures of 500, 700, and 1000°C. According to the silica activity index, the absence of

TABLE 5: BET.

No	Biomass sources	Temperature (°C)	Surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore size	References
1	Teff straw ash	500 @2 hr	52	—	—	[97]
		700 @2 hr	61	—	—	
		900 @2 hr	81	—	—	
3	Teff straw silica gel	750 @2 hr	305	—	—	[98]
4	Rice husk ash	850 @3 hr	72.26	—	—	[129]
2	Rice straw ash	850 @3 hr	94.53	—	—	
6	Corncob ash	850 @3 hr	203.03	—	—	
7	Rice husk ash	700 @5 hr	236.20	0.54	9	[130]
3	Rice husk silica	600 @2 hr	218	0.32	5.56	[131]
4	Sugarcane bagasse ash	550 @1 hr	1.50	0.0049	10.790	[11]
5	Sugarcane bagasse silica		265	0.425	6.250	
6	Coconut husk ash		56	0.14	—	[128]
7	Corncob ash	600 @2 hr	70	0.14	—	
8	Corn husk ash		91	0.21	—	
9	Rice husk ash	800–850	296.98	0.57	7.68	[132]
10	Rice straw ash		413	0.2	1.9	[133]
11	Bamboo leave ash	600@4.5 hr	667.95	58.4	99.97	[134]
12	Rice husk ash	700@4 hr	653	0.64647	1.98	[135]
13	Rice husk silica gel	650@ 6 hr	258		12.1	[76]
14	Sugarcane leaves ash	500@ 4.5 hr	323	0.41	5.0	[8]
15	Maize leaves ash		182	0.34	7.0	

the crystallin phase is largely supported by the lack of strong peaks that would have indicated the absorption of crystal structures that were organized. When rice husk was prepared sustainably at a lower temperature, potassium is found since there are no carbon peaks and the material is porous. In contrast, the rice husk needs to be washed in acid solution prior to thermal treatment in order to primarily remove the potassium content and remove any fixed carbon from the raw materials. The particles' half-width of the peak can be calculated using (3) Scherer's formula. It was found that purity of the biosilica increases with temperature. However, while increasing the temperature amorphous nature of the silica after 700°C was observed to lose, in case of Figure 4(b) by the hydrothermal method, the same was observed as result. In case of Figure 4(a) using the sol-gel method of potential virtually removes all other ingredients, and only amorphous biosilica is formed outside of the temperature range of 500–900°C, according to the XRD pattern [7, 97]. In addition to this, in Figure 4(c) the presence of silica, which is present as crystalline ash is shown by the significant peak detection at 20.9 and 26.6 in section (a). The extracted silica is primarily amorphous, as evidenced by the broad X-ray diffraction pattern in section (b), which is typical of amorphous materials. In general, it has been observed that the diffraction broad peak at theta = 22° suggests amorphous silica together with some crystalline silica in section (c) [111].

4.3. X-Ray Fluorescence Method. X-ray fluorescence (XRF) method is a nondestructive elemental analysis method that can be used for any material. This method is most applicable for pharmaceutical, environmental, forensic, industrial, and different scientific researches areas. XRF is used to determine the elemental concentration of contaminants or constituents based on peak's energy comparison using the element's binding energy. According to scientific research studies, X [140] have reported that the chemical composition of rice husk ash has been determined using XRF technique with sample in oxides forms of silica content of 95.6 wt%, 96.1 wt %, and 95.89 wt% at calcination temperatures of 400, 450, and 500°C, respectively. Based on XRF, it was observed that the commercial biosilica is found to be 98% pure. However, from the teff straw ash, the biosilica was met a good purity up to 92%, while the teff straw ash burnt at 900°C. For teff straw ash obtained at 500 and 700°C, concentration of biosilica was reported to be 85 and 91%, respectively [7].

4.4. Thermo Gravimetric Analysis. Thermo gravimetric analysis (TGA) is a method with modification in mass of samples to be examined through a rise in temperature at quantified with heating rate and vapor environment [141]. In the processing of TGA investigation, the loaded sample with the microbalance arm used for suspension of the small crucible of platinum. The oven temperature can be easily measured and examined. Investigation is supported by rising the temperature of sample, progressively in a flow N_2, Ar, He, and the sample weight can be schemed in contrast to temperature. Heating rate, the quantity of sample, flow of the carrier gas is some of the most affecting parameters. Investigation of materials of volatile, moisture content, and thermal stability are some of the major analyzations based on TGA. TGA techniques can also studied for the determination oxidation, chlorination, hydrogenation, and desorption/adsorption supported with reaction kinetics for
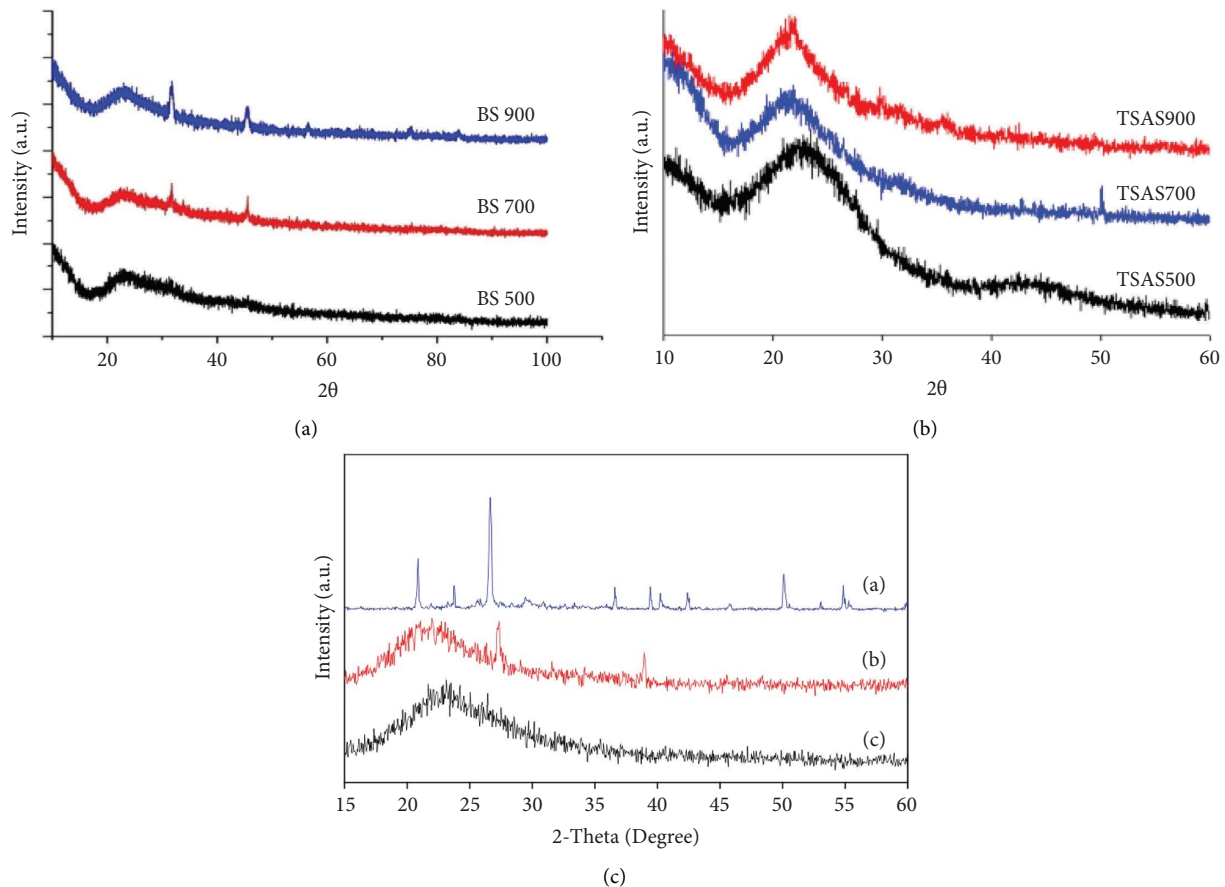
(a)

(b)

(c)

FIGURE 4: Schematic illustration of the XRD of (a) silica gel, (b) silica from teff straw, and (c) corn con ash, silica gel, and nanosilica gel [7, 97, 111].

gaseous reactions. Besides, the TGA techniques study can be applied for pyrolysis kinetics, for example, carbonization and sintering. The TGA analysis have been presented on the mass loss in temperature range of 230–520°C. During this range, the loss is much higher than the temperature range of 520–1000°C. The teff straw ash production was higher from 500 to 700°C than with temperature range of 700–900°C [7].

4.5. Differential Thermal Analysis. Differential thermal analysis works with the same rate of temperature difference between the reference and sample. In DTA analysis, identical thermal condition is used for heating the reference and sample in the same oven. Where on the period of heating, the reference and the sample temperature difference is checked. When the samples are undertaken changes in state, latent heat of the transition will be absorbed the sample temperature is differ from the reference materials. Then, the temperature is recorded for both of reference and sample materials. Along with temperature, the occurrence of change can be detected [142]. Bageru and Srivastava [7] have studied on the biosilica structures obtained from teff straw ash at 700°C. They have demonstrated that the size distribution is not uniform compared with 900°C of teff straw ash.

The derivative profile of DTGA indicates that the temperature rises gives a change of mass loss. Figure 2 presents of the thermograph finds three characteristics conditions in the process of decomposition. There are ranges of mass loss from 25 to 140°C. The initial weight loss upto of 5.87% was occured due to the loss of water. Between 150 and 350°C, the DTGA results have shown the highest peak. In this peak, the area of active pyrolysis was indicated. Gaseous volatiles can be released when hemicellulose and celluloses decomposed into smaller molecules. During this process carbon monoxide and carbon dioxide is released by the reaction carried out for removal of carbon and oxygen eliminated from the polymer materials. Totally, in this process, around 48.05% of the samples mass was eliminated. Between 350 and 500°C, the pyrolysis is called passive. In this stage, 20.14% of mass was out due to the composition process of lignin, so-called passive pyrolysis zone. Studies reported that the 20.14% of mass was released due to lignin combustion at this process. When temperature becomes 550°C the mass becomes stable the content of ash or the inorganic residue [143]. During this stage, the combustion practice happened in three phases: 68–281, 307–381, and 408–454°C. When the first two phases were described by speedy devolatilization, the sample weight lost was from 25.43 to 45.15% this loss was a high considerable amount. In

the DTG curves, the two distinct peak of mass loss indicated, whereas the third phase showed a slow process of degradation [128].

4.6. Methods of Fourier Transforms Infrared Spectroscopy.
Methods of Fourier Transforms Infrared Spectroscopy (FT-IR) is a known as vibrational spectroscopy grounded on the occurrence molecular vibrations that can absorbs infrared radiation. This method provides information about the molecular structure of materials or compounds of functional groups [144]. The oxides and dioxides of the functional groups of biosilica are observed to be nearby 470, 800, and $1100 \, cm^{-1}$. At the temperature of $900 > 700 > 500°C$, as shown in Figure 5(a), the teff straw ash's areas and peak height display increase in corresponding order. In similar way the biosilica concentration order is improved with increasing temperature. Peaks of C=O found on 1400 and $1600 \, cm^{-1}$, C-O on $2350 \, cm^{-1}$, C-H on 2860, and $2930 \, cm^{-1}$ were detected as unburned with peak strength order these is due to the impurity of carbon. It is apparent that while increasing the temperature impurity of the carbon was also increased. The spectra with peak of all samples visibly show similar positions. In the same way which includes around $1100 \, cm^{-1}$ have a strong band, around $800 \, cm^{-1}$ have a sharp band of medium and on around $470 \, cm^{-1}$ have a strong band Si-O-Si asymmetric vibration have a strong absorption peaks at $1100 \, cm^{-1}$ and the higher ionic character of the Si-O group have a shear bands [7]. The symmetric stretching of vibrations of SiO_4 tetrahedral is due to the band at $800 \, cm^{-1}$ and the Si-O bending band vibrations occurred due to at $470 \, cm^{-1}$ [146]. The asymmetric stretching is found on the broad band between 3000 and $3700°C$ and whereas the silanol of O-H groups absorptions of the vibrations of bending in most of the time caused by physical absorption of water [147]. According to Figure 5(b), the vibration network of O-Si-O is connected to the band $463–475 \, cm^{-1}$, while the symmetric stretching vibration network of O-Si-O was assigned to the band $791–807 \, cm^{-1}$. Broadband at $1633–1645 \, cm^{-1}$ is due to O-H bond bending vibration from Si-OH silanol groups, while $3338–34,750 \, cm^{-1}$ is due to O-H bond stretching vibration from Si-OH silanol groups and are due to adsorbed H_2O molecules on the silica surface. Band $1071–1090 \, cm^{-1}$ was due to Si-O-Si irregular stretching vibration [145].

4.7. Methods of Raman Spectroscopy.
The vibration and rotation modes of molecules were studied by Raman spectroscopy. Based on the Raman spectroscopy of each compound have exceptional spectrum for the case of the cross-reference. On the sample of the analysis a laser light is focused which is due to the vibration of molecule. Because of light scattering that results in shifting either down or up for the energy of photon laser will be in the form of excitation [148]. This method can be used for analyzing crystals and molecules of the internal structure [138]. This all based on phenomenon of scattering of electromagnetic radiation is carried out by molecules. Elastic or inelastic scattering is performed by molecules [138, 148].

4.8. Methods of Transmission Electron Microscopy.
Transmission electron microscopy is a system detecting membrane surface. The magnification of TEM is around of 50 million which is suitable for nanometer scale measurements and more magnification compared with SEM [137]. Based on TEM information can the analysis can be made on surface area and texture-based topography, shape, and size of the particles based on morphology, arrangements of atoms of crystallographic, and elements and their relative amounts base on composition.

Rajaeiyan and Bagheri-Mohagheghi [149] have studied on nanoparticles of the image using TEM was carried out. The particles were synthesized by sol-gel and coprecipitation techniques strengthening at $1250°C$. The alumina particles produced by coprecipitation system had the size of 10–50 nm of diverse shape which have been looked hexagonal of irregular or spherical. But, form the sol-gel method, having the size scattering of 10–20 nm showed more spherical which is for the case of nanoparticles of alumina.

4.9. Scanning Electron Microscopy.
For analysis of membrane the morphology and topography data of the prepared membranes SEM is one of the essential methods. Additionally, for the case of porous material to determine the pore size method of SEM is most preferable one. In case of a compressed membrane to measure thickness of the selective layer SEM can be the appreciable method. In SEM, samples should be in form of solid and moisture free. Samples moisture can be evaporated because it works under vacuum and also the sample is electrically conductive if not coating by metallic component is preferable [137]. For dealing the electron microscopic structure SEM is the most used method. Surface area of the specimen can be scanned for focusing the formed image based on SEM technique. In this technique, the electron beam is also called as incident beam where 10 nm is detected. Furthermore, $1 \, \mu m$ and also in SEM instantaneously image is not formed where illuminating the whole part with a similar fashion with TEM. When the sample must be made thin in TEM for electron transition otherwise it will be scattered or absorbed. In nutshell, the SEM technique can overcome for this limitation [137, 138]. During the studies by Rajaeiyan and Bagheri–Mohagheghi [149], the particles image formed based on SEM from the analysis of the methods of sol-gel and coprecipitation was analyzed. In coprecipitation method strong agglomeration and varied size of the particle is formed where as in case of sol-gel method the particles showed a uniform particle distribution as well as elongated shape. Therefore, in sol-gel method the structure of gelatinous state is formed from the precursor which allowed alumina crystalline of free from agglomeration.

The SEM pictures in Figure 6 clearly reveal a difference, which can be seen in the textures of the biosilica samples prepared from teff straw. For example, in Figure 6(a) at $500°C$ particles' darker colour and larger size indicate the presence of carbon impurities that were left behind in the sample after incomplete combustion at $500°C$ compared
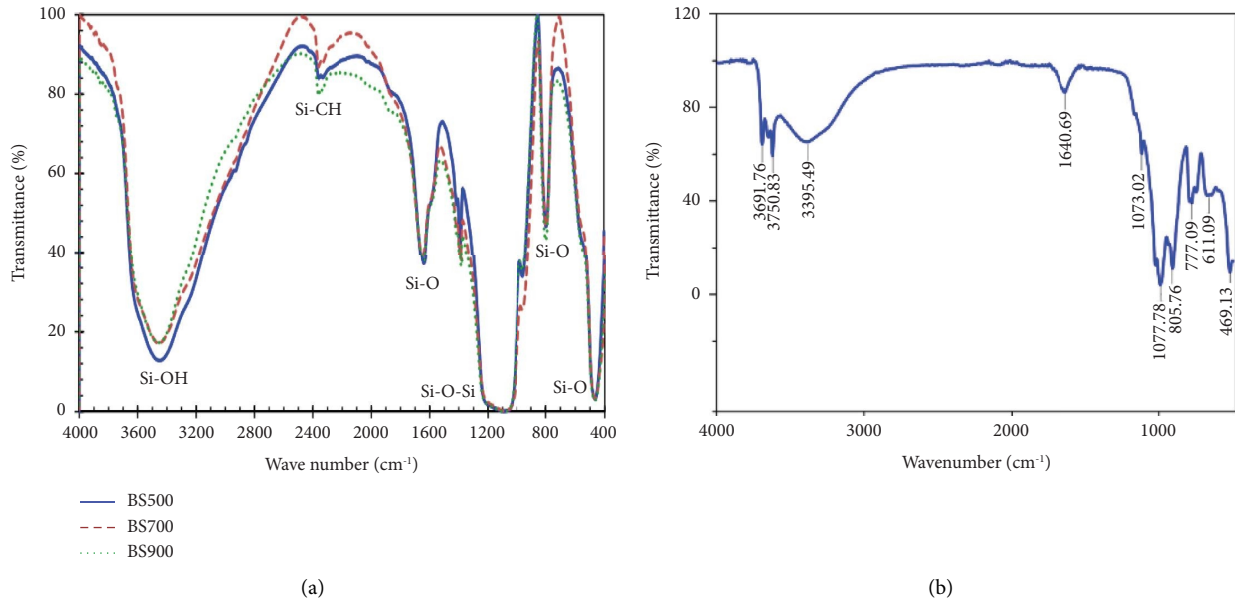
(a)

(b)

FIGURE 5: FTIR spectra of samples of biosilica produced synthetically from teff straw (a) [97] and palm kernel shell (b) [145].

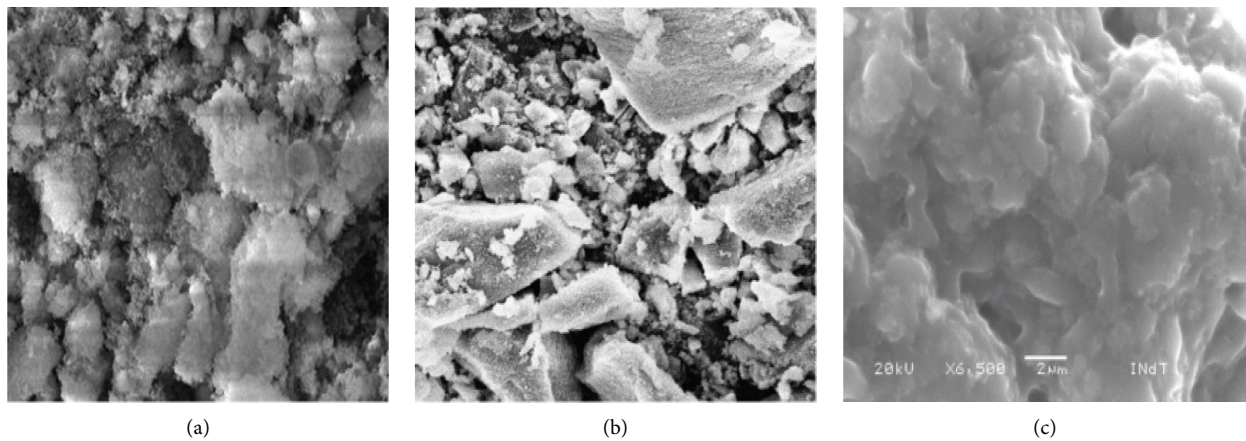(a)   (b)   (c)

FIGURE 6: SEM examination of samples of biosilica made from teff straw (a) and (b) synthetically [97] and (c) silica gel from rice husk [15].

with biosilica prepared in Figure 6(b) at 700°C [97]. The micrograph of the rice husk ash instance demonstrates that individual silica grains were not visible. Instead, the silica formed uneven and cohesive surfaces by clustering into spherical clusters [15].

5. Applications of Silica Gel

Silica gel is one of the most significant inorganic materials that have been broadly known for stable and desirable properties with respect to temperature and mechanical influences [12]. Silica gel has been exploited potentially for raw materials to produce silicon carbide and soluble silicates. Both of these materials are used in different applications such as ceramics, electronics components, refractory industries, manufacture of glass, rubber tire filling material, chromatographic stationary phase, adhesive, components in the ceramic, detergent, and pharmaceuticals. As we know,

the price of mineral silica is quite expensive. Hence, the use of biosilica has become better alternative for silicon chip manufacturing [13]. Hence, it needs an effective production of high value-added biosilica from a low-cost material that can be an alternate way compared with the conventional production method. Some of the major applications of silica gel were presented as follows.

5.1. Applications of Nanosilica. Recently, a significant amount of silica has been extensively used in different industries. In specific, nanostructured silica has a potential characteristic that is required for recent applications [150] for biosensors, bioimaging, drug delivery systems [3], drinking water, and wastewater treatment [46], CO_2 capture applications [151, 152], superhydrophobic coatings [153], toothpastes as a cleansing agent, reinforcing agent, anti-caking agent in salts, cosmetics applications [11], uses as

a catalytic support in acetic acid steam reforming [19], in agricultural and environmental remediation potential applicability [38], and so on. In other, silica gel is commonly applied to absorb excess moisture present in the environment. It is put forefront of refrigerant drying, process industries, insulating glass industry, desiccant powder, and packaging desiccants [106]. Silica gel desiccant in sachets is considered to have a scavenger property for water [105].

Utilizing silica nanoparticles as reinforcement or filler in sophisticated composite materials is one of their most well-known uses. The capacity to achieve homogeneous filler dispersion, which affects how well silica-polymer nanocomposites perform overall, is one of its key features [121]. An essential step in preparing silica-polymer nanocomposites is the chemical modification of silica surfaces with organofunctional groups. It has been noted that surface changes promote the dispersion of silica nanoparticles inside the polymer matrix while also improving the affinity between the organic and inorganic phases [154]. In the concrete industry, silica nanoparticles have the potential to solve numerous technical problems relating to concrete materials and significantly improve the mechanical characteristics of concrete [155]. This nanomaterial also has effective since it has a significant pozzolanic activity [156]. Concrete and mortar materials can be benefited from the microstructure-improving effects due to the colloidal silica nanoparticle attachment [157].

5.2. Chemical Applications of Silica Gel.
Typically, trialkoxysilanes with organo-substituted co-condensation or post-synthesis grafting are used to functionalize silica particles [158]. For instance, one of the most often used metals functionalized onto mesoporous silica nanoparticles for catalytic applications is aluminum. It was utilized to deliver drugs [159]. Titanium oxide and iron oxide are incorporated in produced silica nanoparticles. The synthesized substance was utilized in catalytic processes [160]. Silver nanoparticles based on silica have recently been created and will be utilized to treat *Mycobacterium tuberculosis* [161]. Similar to this, copper, silver, and copper hydroxy salt were employed to create the corresponding metallic silica nanoparticles, which displayed positive and encouraging outcomes when used as antibacterial agents [162].

5.3. Biomedical Application of Silica.
A widely acknowledged characteristic currently being researched is the use of tailored nanostructures for the targeted administration of medications to patients [38, 163]. These nanostructures can serve as transporters and direct substances to particular organs or human tissues. Due to their large surface area and porous structure, mesoporous silica nanoparticles have gained considerable respect in this regard. Recently, these particles have been utilized as nanocarriers for the delivery of medications [164]. Additionally, the hydrophobicity of the medicines decreases absorption during oral administration. This is enhanced by utilizing silica nanoparticles as carriers for such hydrophobic medications, which have

demonstrated encouraging outcomes when administered orally [163].

5.4. Agricultural Applications.
A bioactive component called silica has been linked to fungicidal effects. Different investigations revealed that silica could increase the resistance against fungal diseases. It has been proven that the environmental stress and tolerance can increase; in nut shell, the productivity of crop significantly improves [165]. It has been demonstrated to boost the resistance of cucumbers to powdery mildew [166], in cucumbers and grapes [167, 168]. In the recent past, in vitro studies have also been performed to investigate the antifungal effect of silica, and in vitro inhibition of mycelial growth of several phytopathogenic fungi grown on potassium silicate amended media has been reported [165].

5.5. Applications for Food Preservation.
Many fruits can be coated with hybrid films made of silica to extend their shelf life and keep fresher for longer [169]. It has been demonstrated that some fruits can prolong their shelf life dramatically. Fruit has a tendency to make you lose weight, better enzymatic activity, more reducing sugars, and a longer shelf life [170]. The addition of nanofillers such as silicate, clay, and titanium dioxide to biopolymers may enhance their mechanical and barrier qualities as well as provide additional uses as an antibacterial agent, biosensor, and oxygen scavenger in food packaging [171]. The bio-nanocomposite can be utilized as an active food packaging that can interact with the food in a number of ways, such as by releasing beneficial components such as antibacterial agents and antioxidant agents or by eliminating unfavorable factors such as oxygen or water vapor. Additionally, the bio-nanocomposite can be employed as smart food packaging that detects the features of the packaged food, such as microbial contamination or expiration date, and uses a mechanism to record and convey information about the product's quality or safety [170].

5.6. Industrial Applications.
Silica nanoparticles are ideal for a variety of industrial applications due to their mesoporous structure and high surface area. Due to the exceptional qualities these particles exhibit, more and more people are turning to these applications. As an illustration, mesoporous silica-based nanofibers have demonstrated remarkable potential for immobilization and are thus an appropriate material for encapsulation [172]. Moreover, by encapsulating capsaicin using the same fiber matrix, the enzyme's stimulation activity was increased. This demonstrates the viability of employing mesopore silica nanoparticle fibers used for enzymatic encapsulation [173].

5.7. Environmental Applications.
Due to their toxicity, inability to degrade, and long-lasting nature, heavy metals such as arsenic, copper, cadmium, chromium, nickel, zinc, lead, and mercury are important contaminants of fresh water reservoirs. These heavy metal ions are naturally present in the environment, but due to an increase in

industrial waste, their concentration is rising right now [174]. The harmful ions get into the food chain and ultimately get into people [175]. For instance, consuming too much zinc may result in health issues such as stomach pains, vomiting, and skin irritations, Ni concentrations above a certain level cause lung and kidney cancer [176]. Natural zeolites, naturally occurring silicate minerals, have been utilized extensively in place of manufactured resins to remove heavy metals from aqueous solutions due to their inexpensive cost and high availability [177]. Moreover, compared to controls, silica nanoparticles exposed to polluted plants absorbed more air lead [178].

5.8. Applications in Water Purification. Using silica nanoparticles, heavy metals can be removed from aqueous solutions. The same has already been demonstrated in a number of studies, supporting its use in the treatment of industrial effluent [179]. Additionally, silica nanoparticles have been demonstrated to reduce or completely eliminate the biological oxygen demand (Sahebi et al.). Compared to more traditional approaches that do not use silica nanoparticles, biological oxygen demand (BOD) activity is more effective [180]. To test their antibacterial effectiveness, synthetically made silver nanoparticles were mixed with silica nanoparticles. Furthermore, the temperature and organic matter content of nanoparticles had a significant impact on their antiviral activity. According to the study, silica linked nanoparticles may be used as antivirals to destroy viruses in wastewater [181].

5.9. For the Application of Semiconductor. The main component of the solar cell's semiconductor layer may be silica. The semiconductor is a substance with conductivity that is between that of an insulator and that of a conductor. The bandgap energy is the primary factor that determines how a semiconductor interacts with other materials. The difference between the valence band and the conduction band section, which defines the amount of transition energy required to convert the electron band from the valence band to the conduction band, is determined by the energy bandgap [182]. Bandgap energy for semiconductors ranges from 0 to 4 eV, whereas it is beyond 4 eV for isolators and below 0.5 eV for conductors [183]. Due to the leaps made by excited electrons, semiconductors are created as materials that support electric currents. The photovoltaic principle states that silicon crystalline base material is used to create solar cells because of its abundance, lack of toxicity, and high conversion efficiency [184].

6. Conclusions and Future Prospects

In this review paper, synthesis, characterization mechanisms, and application areas of biosilica were reviewed. Agricultural waste resources such as palm tree, wheat straw, maize leaves, teff straw, sugarcane bagasse, rice husk, rice straw, sugarcane leaf, oat husk, bamboo leaf, and corn cob can be used as a source of silica was presented. From these biomass sources, using different approaches such as sol-gel, hydrothermal, chemical vapor deposition, impregnation, electrodeposition, coprecipitation, and leaching method synthesizing of silica gel have been described briefly. Then, using different characterization mechanisms such as BET, XRD, TEM, and SEM were presented. Also, the multipurpose applications used in the form of catalyst, synthesis of shear thickening fluid, chemically inert material, strong adsorption capacity, ceramics, concrete materials, glass, cement, medicine, supercapacitors, batteries, cosmetics, detergents, adhesive agents, pharmaceutical, fine-chemicals, clean fuels, catalyst support, microfilters, thermal super-insulation, controlled release of drugs, and good option to deliver drugs of antibiotics were presented here. This review indicates that the results from agricultural wastes source of silica is an alternative one. Therefore, this form of silica basis will contribute benefits used for a low-cost input material, pure silica product, and environmentally-friendly.

Besides these, the subsequent features have a necessity to be addressed in upcoming mechanisms: (1) advance studies on agricultural leftover resulting biosilica in order to grow better-quality fresh adsorbent on behalf of removing organic and inorganic wastes from drinking and wastewater. (2) Development of a high-yield and cost-effective biosilica which replace an energy-intensive commercial sale product. (3) Biosilica products have their own merits such as the raw materials that are easily available, cost-effective, pure yield, and environmentally-friendly. (4) The merits and demerits of each preparation method of biosilica are still not clear. Consequently, scientists are quite challenged with incomplete consideration in this zone of biosilica preparation. On behalf of the advance argument on this fact of view, the reader can denote the reference presented now. (5) In emerging requirements for silica, there is an essential behalf of critical care over the outline of favourable directive that encourages the vast usage of used yields after leftover.

Data Availability

All data used in the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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