



Crop Residues as Potential Sustainable Precursors for Developing Silica Materials: A Review

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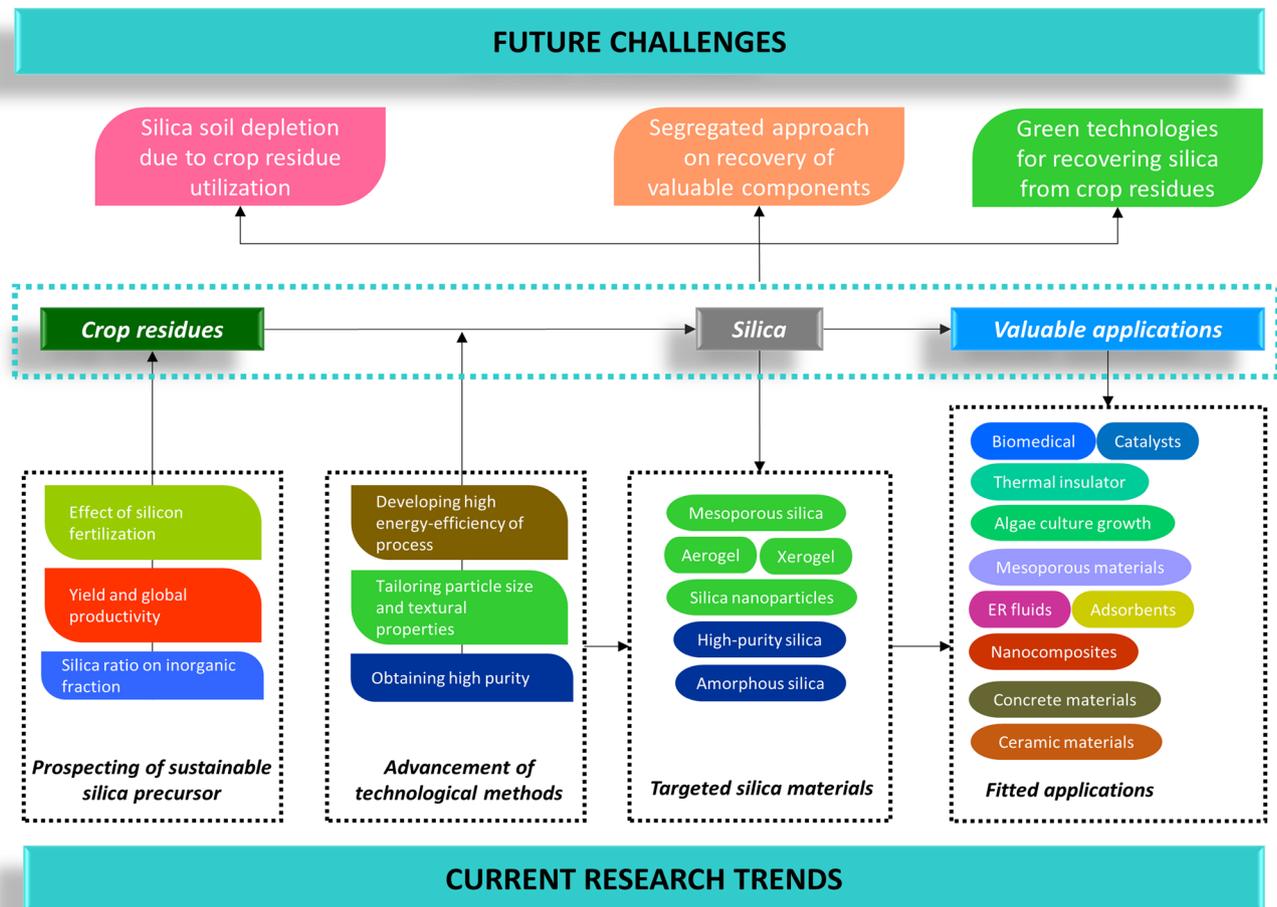
Abstract

Prospecting for sustainable resources will be feasible to generate silica materials extensively used for various commercial applications. Accumulated amorphous silica, called phytolith, is found in the crop residues removed during the harvesting process. Hence, it will be beneficial to understand the potential for various kinds of crop residues used as silica production resource regarding their global generation, yield of generation, and enhancement using silicon fertilizer. Of the many crop residues discussed in this study, sugarcane leaves are the most useful potential silica source. Various synthesis methods are continuously developed with the expectation to achieve tunable silica particle properties with high processing efficiency. The applications for silica particles derived from crop residues vary depending on their unique characteristics related to textural and morphological properties. Silica materials developed from crop residues present several challenges involving silica depletion in croplands, segregation of valuable components from crop residues, and the high utilization of high energy and chemical reagents. Utilizing industrial wastes containing silica can be promoted as Si fertilizer to heal silica depletion in croplands. An integrated approach can be conducted applying low energy with fewer chemical methods to recover energy, lignocellulosic materials, carbonaceous materials, and siliceous material from crop residues, simultaneously.

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Graphic Abstract



Keywords Silica · Crop residues · Sustainable development · Simultaneous recovery

Statement of Novelty

The novelty of the present paper is a comprehensive review on the development of crop residues-derived silica materials with typical characteristics for numerous valuable applications. Furthermore, the future challenges are also discussed encompassing silica soil depletion due to crop residues utilization, simultaneous recovery of valuable components from crop residues, and employment of eco-friendly technologies to recover silica from crop residues.

Introduction

Rapid global population growth promotes the sustainable production of crop plants to fulfill global food demand [1]. The generation of residues after harvesting process will be proportional to the productivity of crop plants. High

abundance of those crop residues must be handled by applying compatible technological processes to recover their valuable components. Many technologies have been employed to utilize crop residue organic components that generate renewable energies [2–29], carbonaceous materials [30–45], and lignocellulosic materials [7, 46–56]. However, it will be more advantageous to accomplish utilization by recovering inorganic matters in ash residues that mainly consist of silica.

Silica is well known as a precursor for many applications such as catalysts [57–61], electronic coating [62–66], ceramics [67–71], concrete [72–76], chromatography [77–81], anticorrosion agent [82–85], and optic materials [86–90]. The employment of high purity silica in industrial applications will be costly due to the high processing temperature [91, 92]. Thus, the silica synthesis from crop residues will be a good option to reduce the processing costs and counter sustainability challenges. Due to high requirement for silica

particles for industrial applications include high purity and controllable textural properties. The applicable residues must be subjected to the appropriate technological processes to obtain targeted silica products.

The silica extraction method relies on thermal [92–110], physical [111–115], chemical [91, 99, 106, 108, 110, 116–136], or even biological processes [95, 137, 138] to obtain silica from crop residues. The typical compositions of inorganic fractions in crop residues require specific technological methods to obtain silica particles. Moreover, those methods will determine the physical, morphological, and textural properties of the synthesized particles. Therefore, it will be beneficial to classify various silica extraction methods based on their conception and the advancement toward green, high energy efficient processes.

Various silica materials can be generated from crop residues such as amorphous silica powder [7, 46, 91, 95, 101–105, 107, 109, 117, 122, 123, 128, 133, 139–147], silica nano particles [108, 115, 118, 119, 124, 127, 131, 134, 135, 148–152], silica xerogel [116, 126], silica aerogel [120, 125, 132, 153], mesoporous silica [154–156], and microsphere silica [129, 157–159]. Siliceous materials-based crop residues are widely applied in pollutants removal by absorption and adsorption, drug delivery in biomedical applications, cement and ceramic based materials, catalysts for many transformation processes, and fillers in composite/membrane fabrication. The expansion of applications for these silica materials is certainly required to achieve sustainability in the future. Therefore, in-depth analysis can be considered to specify various constraints and opportunities to develop sustainable silica recovery from crop residues.

This study explores crop residues that have high potential as silica sources, summarizes recent technological processes for recovering and generating derivative silica products, and specifies silica applications from crop residues based on their textural properties. Challenges and future recommendations for developing silica materials from crop residues are also discussed.

The Crop Residue Advantageous Factors as Silica Precursors

Silica as a Major Inorganic Constituent in Crop Residue

Silica has received high attention for agricultural practices due to its beneficial impacts for improving the yields and qualities of a large group of crops. Those beneficial impacts are strongly associated with silica accumulation behavior which differs by plant species. Agricultural plants classified as monocotyledons such as rice (*Oryza sativa*), wheat (*Triticum aestivum*), ryegrass (*Lolium perenne*), maize (*Zea mays*), barley (*Hordeum vulgare*), banana (*Musa sp.*) and some cyperaceous plants were believed to take up and deposit more silica through active transport [160]. Active transport allows more silica trans-membrane movement due to the presence of Si transporter proteins such as poly-2-vinyl pyridine-1-oxide located at the plasma membrane. Figure 1 illustrates the silica uptake mechanism and its impact on agricultural plants. Silica serves as insoluble crystalline aluminosilicates in soil that cannot be taken up by root plants

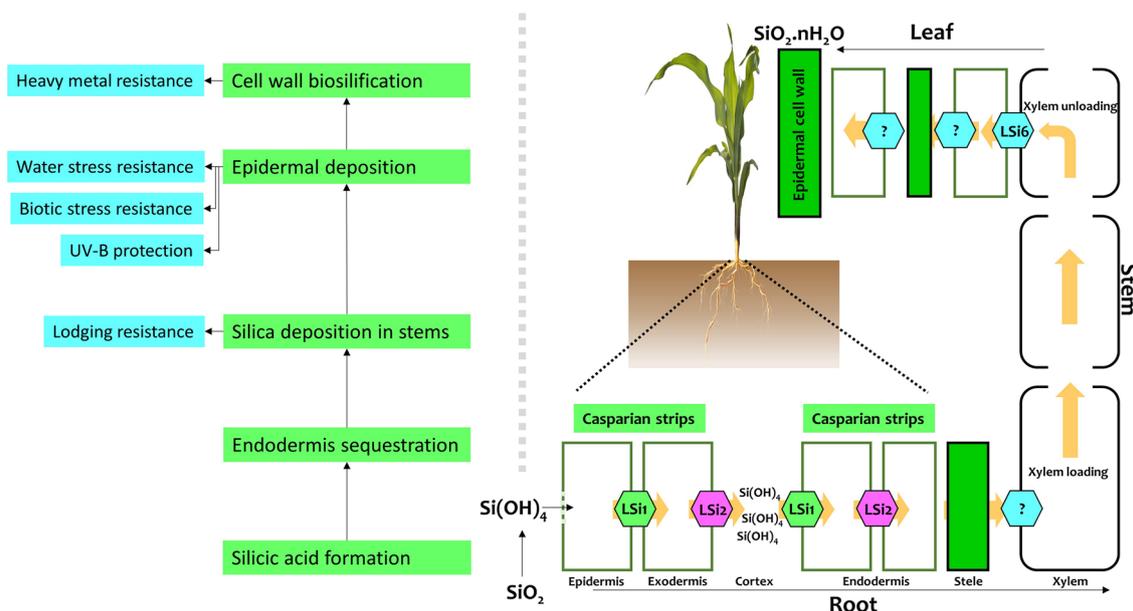


Fig. 1 Silica accumulation and its impact on agricultural plants, adapted from Luyckx et al. [163] and Khan et al. [164]

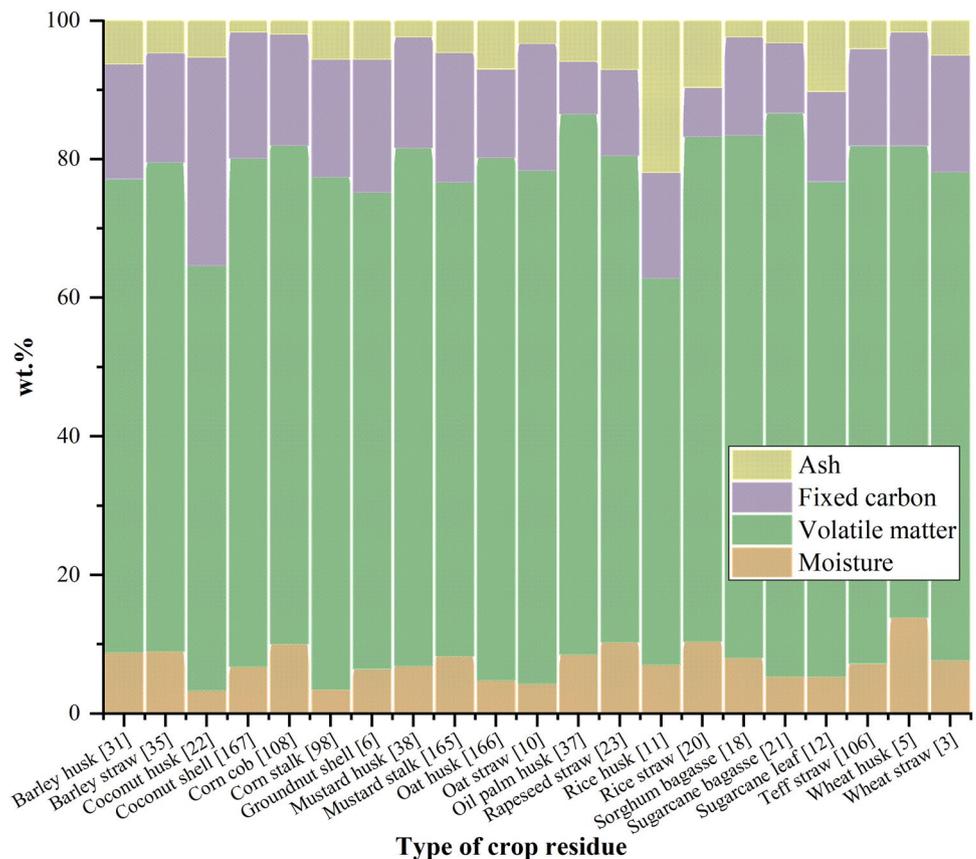
[160]. This primary silicate mineral can be weathered and desilicated to liberate dissolved silicon in the form of silicic acid. Silicic acid is taken up from the external solution and released into the aerenchyma apoplast, and then transported into the stele [161]. It is then translocated into the shoot by stream transpiration through the xylem. Due to large water loss, silicic acid is further concentrated and then polymerized into an amorphous silica phase without any energy higher than 2 mol L^{-1} of concentration [161]. The proportions and locations of amorphous silica vary with the plant species and age of plants. In some cases, amorphous silica can be found in the epidermis of leaves, seeds and fruit of trees and herbs and the tissues of leaf blades and inflorescence bracts in grass plants [162]. Mature plants are believed to possess the largest portion of deposited amorphous silica due to the irreversible silica deposition process in older cell walls.

During the harvesting process, crop residues in the form of husks/hulls, straw/stalks, leaves, and bagasse are removed from croplands. The proximate analysis and chemical composition of ash can be considered to determine the silica content of these residues. Twenty-one crop residues from 13 agricultural plants are discussed in this study. As shown in Fig. 2, crop residues generally possess 3–14% of moisture, 60–86 wt% of volatile matter,

8–31 wt% of fixed carbon, and 2–22 wt% of ash [3, 5, 6, 10–12, 18, 20–23, 31, 35, 37, 38, 98, 106, 108, 165–167]. These properties indicate high potential of crop residues for producing gaseous energies through thermal decomposition process. In term of ash content, several crop residues such as rice husk, rice straw, and sugarcane leaf exhibit exceptional values in the range of 10–22 wt%. Higher ash contents will be advantageous for recovery process of prominent inorganic species in crop residues.

Silica exists in the ash residues of agricultural plants, accompanied by various oxide forms of metal and alkali such as Al_2O_3 , Fe_2O_3 , MnO , ZnO , CuO , Sr_2O_3 , TiO_2 , K_2O , CaO , MgO , Na_2O , etc. [35, 92–94, 96–100, 103, 108, 110, 168–173]. The SiO_2 content in crop residues varies in the large interval of 9–93%. Some dicots classified as intermediate Si-accumulating plants such as groundnut, mustard, and rapeseed, exhibit lower SiO_2 content up to 50 wt%. Meanwhile, crop residues from monocots such as barley, corn, oat, rice, sorghum, and wheat tend to comprise high silica concentrations ranging up to 90 wt% due to their active silica uptake. Silica is more concentrated in pericarp cells rather than stem cells, since the beneficial impact of silica in providing a physical defense by creating a firmer/stiffer structure in seeds, grain, beans, or kernels. In these regards, it will be reasonable for wheat husk and

Fig. 2 Proximate analysis of various crop residues



rice husk, exhibiting high SiO_2 content at 92.30 % and 91.25%, respectively (Fig. 3).

The existence of metal and alkali species in crop plants is related to their role as essential or nutritious elements for plants. The alkali elements K, Ca, Mg are generally classified as macronutrients while metal elements Fe, Mn, Cu, Zn are supposed to be micronutrients. The alkali oxide contents in crop residues are varied in the large interval of 5–64%. High concentration of alkali oxides is observed on residues of crop plants with low or intermediate Si-accumulation such as mustard husk, rape straw, and groundnut shell. In contrast, low concentration of alkali oxides is typical for residues of monocots especially rice and wheat. It indicates that higher silica uptake may interfere the existence of alkali oxides in crop residues. On the other hand, the content of metal species in crop residues varies in the extremely low interval of 0.9–15%.

Classified Prospect Crop Residues as Silica Source

Determining the prospects of silica precursors can be carried out by considering both the silica yield and productivity which can be derived from crop residues as seen in Table 1. These parameters will determine the sustainability of crop

residues as an affordable silica precursor. The productivity will be associated with extractable silica and harvested area whereas the silica yield from each crop residue is determined by considering the residue ratio, ash content, and silica ratio in ash.

As shown in Table 1, rice straw and rice husk possess the highest silica yield; as much as 76 g silica/kg crop and 40 g silica/kg crop, respectively. By considering those values and the global production of rice, the value of extractable silica from rice straw and rice husk is in the range of 28,000–55,000 million kilograms per year. Although sugarcane leaf has lower silica yield than rice straw and rice husk, high sugarcane productivity can promote adequate extractable silica at approximately 37,000 million kilograms per year. Once the harvested area is considered, sugarcane leaf will be the best agricultural residue for generating silica with 1415 kilogram per hectare, followed by sugarcane bagasse, rice straw, rice husk, and oil palm husk. The other crop residues originating from barley, coconut, corn, oat, rapeseed, sorghum, and wheat have relatively lower silica yield.

In general, the straw residues provide high yield and productivity compared to that of husks. For instance, the wheat straw generates a yield up to 34 g silica per kg crop, higher than that of wheat husk with approximately 3 g

Fig. 3 Ternary phase diagram of ash chemical composition of various crop residues

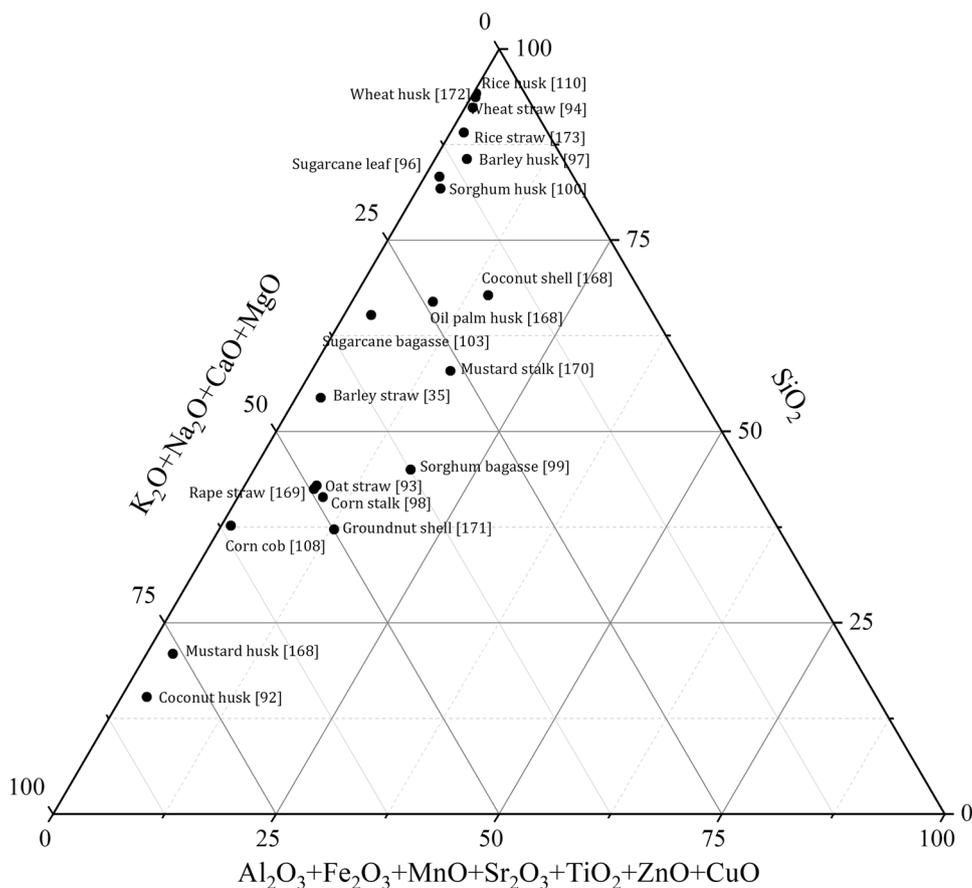


Table 1 Global generation and yield of extractable silica from several crop residues

Type of crop residue	Residue ratio (kg residue/kg crop)	Ash ratio in residue ^a (g ash/kg residue)	Silica ratio in ash ^b (g silica/g ash)	Silica ratio in residue ^c (g silica/kg residue)	Yield ^d (g silica/kg crop)	Crops production ^e (million tons crops/year)	Extractable silica (million kg silica/year)	Harvested area ^e (million ha)	Productivity (kg/ha year)
Barley husk	0.20 ⁽¹⁾	61.79	0.85	52.53	10.51	141	1481.23	47.01	31.51
Barley straw	1.00 ⁽²⁾	45.57	0.45	20.47	20.47	141	2886.48	47.01	61.40
Coconut husk	0.35 ⁽³⁾	52.00	0.09	4.80	1.68	61	102.58	12.3	8.34
Coconut shell	0.35 ⁽⁴⁾	16.20	0.67	10.81	3.78	61	230.87	12.3	18.77
Corn cob	0.16 ⁽⁵⁾	19.06	0.34	6.54	1.05	945	988.42	197.19	5.01
Corn stalk	0.50 ⁽⁶⁾	55.00	0.35	18.98	9.49	945	8965.69	197.19	45.47
Groundnut shell	0.30 ⁽⁷⁾	55.00	0.35	19.39	5.82	43	250.17	27.94	8.95
Mustard husk	0.20 ⁽⁸⁾	23.00	0.17	4.01	0.80	0.58	0.47	0.62	0.75
Mustard stalk	0.70 ⁽⁹⁾	45.19	0.54	24.54	17.18	0.58	9.96	0.62	16.07
Oat husk	0.25 ⁽¹⁰⁾	69.40	0.83	57.53	14.38	23	330.77	10.2	32.43
Oat straw	0.77 ⁽¹¹⁾	32.10	0.38	12.13	9.34	23	214.83	10.2	21.06
Oil palm husk	0.35 ⁽¹²⁾	58.00	0.63	36.66	12.83	256	3284.38	21.35	153.84
Rapeseed straw	0.67 ⁽¹³⁾	69.90	0.41	28.52	19.11	65	1242.01	34.74	35.75
Rice husk	0.20 ⁽¹⁴⁾	218.90	0.91	199.75	39.95	723	28,883.31	167.24	172.71
Rice straw	1.00 ⁽¹⁵⁾	95.60	0.80	76.31	76.31	723	55,170.63	167.24	329.89
Sorghum bagasse	0.30 ⁽¹⁶⁾	23.00	0.40	9.24	2.77	62	171.80	40.67	4.22
Sorghum husk	0.15 ⁽¹⁷⁾	40.00	0.78	31.28	4.69	62	290.87	40.67	7.15
Sugarcane bagasse	0.30 ⁽¹⁸⁾	31.00	0.53	16.46	4.94	1788	8829.68	25.98	339.86
Sugarcane leaf	0.25 ⁽¹⁹⁾	102.60	0.80	82.22	20.56	1788	36,753.97	25.98	1414.70
Wheat husk	0.20 ⁽²⁰⁾	16.00	0.92	14.77	2.95	699	2064.57	218.54	9.45
Wheat straw	0.78 ⁽²¹⁾	48.92	0.88	43.09	33.61	699	23,495.03	218.54	107.51

^aData referred from Fig. 2

^bData referred from Fig. 3

^cObtained as a result from computation of ash ratio in residue \times silica ratio in ash

^dComputed as a result from residue ratio \times silica ratio in residue

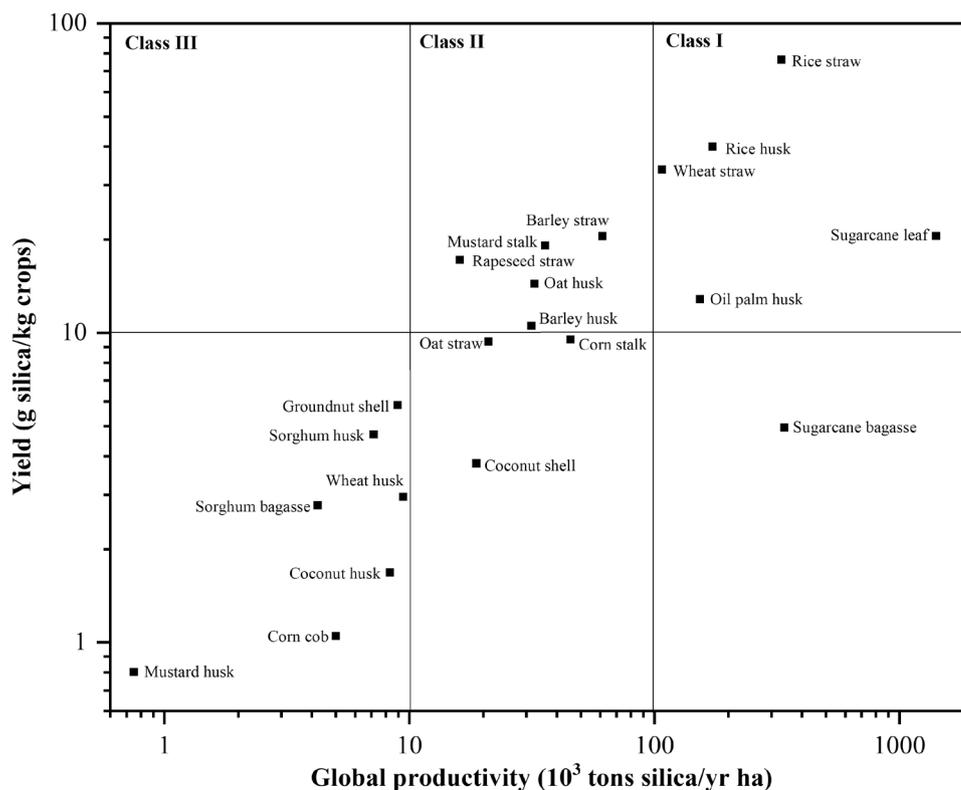
^eCollected from FAOSTAT, <https://www.fao.org/faostat/en/#data/QC>

⁽¹⁾Loredo-Cancino et al. [31]; ⁽²⁾Pallares et al. [35]; ⁽³⁾Anuar et al. [92]; ⁽⁴⁾Islam et al. [32]; ⁽⁵⁾Miranda et al. [174]; ⁽⁶⁾Zhang et al. [175]; ⁽⁷⁾Perea-Moreno et al. [14]; ⁽⁸⁾Assumed to be similar with barley husk; ⁽⁹⁾Maiti et al. [176]; ⁽¹⁰⁾Thomson et al. [177]; ⁽¹¹⁾Kim et al. [2]; ⁽¹²⁾Assumed to be similar with coconut husk; ⁽¹³⁾Ai et al. [178]; ⁽¹⁴⁾Azat et al. [110]; ⁽¹⁵⁾Lim et al. [4]; ⁽¹⁶⁾Appiah-Nkansah et al. [16]; ⁽¹⁷⁾Chandrabu et al. [179]; ⁽¹⁸⁾Anukam et al. [8]; ⁽¹⁹⁾Kumar et al. [180]; ⁽²⁰⁾Bledzki et al. [181]; ⁽²¹⁾Azocar et al. [182]

silica kg crop of yield. It indicates that residue ratio will be more significant to establish a higher yield rather than silica ratio. Furthermore, the amount of extractable silica and productivity will be proportional with ash ratio in crop residues. Thus, crop residues with higher ash content will provide higher sustainability of silica production.

Figure 4 presents the data plots for yield and productivity to classify the prospects of various types of crop residues as a silica source. Class I encompasses crop residues with high residue ratio and ash content which can generate high yield and productivity. Rice straw, rice husk, sugarcane leaf, wheat straw, and oil palm husk are identified as Class I

Fig. 4 Prospecting crop residues based on their silica yield and global silica productivity (data plotting from Table 1)



crop residues with high prospects for silica recovery. Class II represents crop residues with high residue ratio and low ash content. Barley straw, mustard stalk, rapeseed straw, oat husk, barley husk, oat straw, corn stalk and coconut shell are classified as class II with intermediate silica recovery priority. Crop residues with low productivity and silica yield are grouped into Class III, including groundnut shell, sorghum husk, wheat husk, sorghum bagasse, mustard husk, coconut husk, and corn cob.

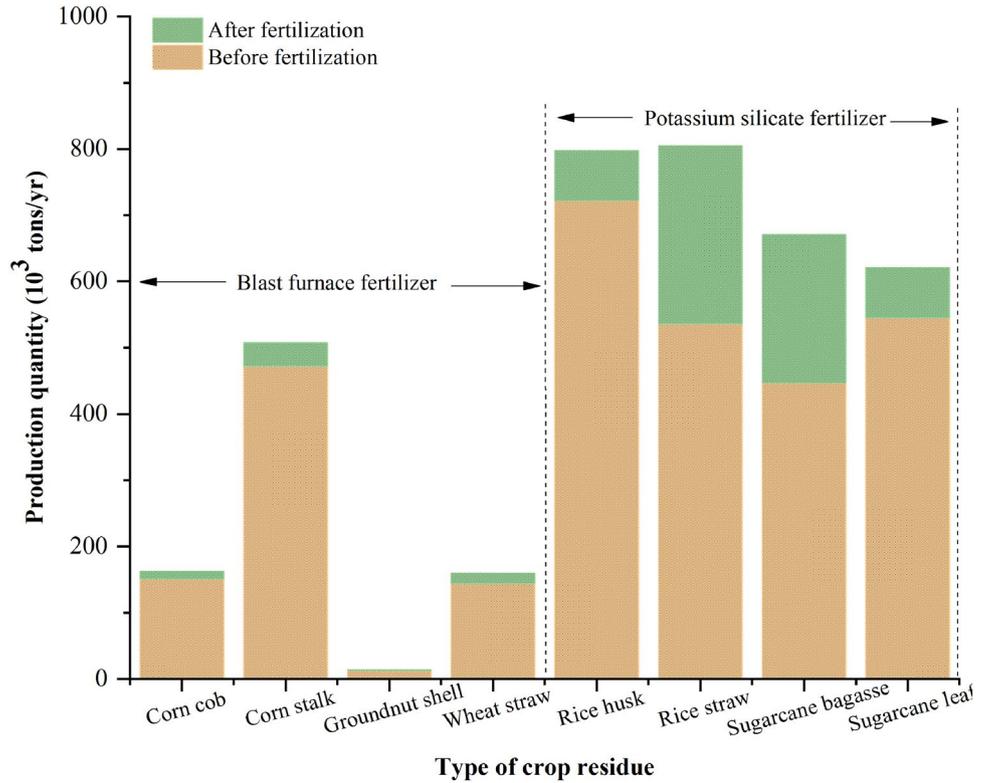
Effects of Silicon Fertilizer

Silicon is known as a beneficial plant nutrient that serves as a protective system from biotic (pests and diseases) and abiotic stresses. The tolerance against pests and diseases is available due to the interaction between the host and the pathogen associated with the presence of silicon along with a certain defensive response by plants. Silicon deposition in plants also improves the abrasiveness of the plant tissues which could prevent herbivores and arthropods from digesting plant bodies rich in silicon [183]. Abiotic stress resistance could be defined as the ability to exert resistance to unexpected conditions mainly due to extreme climate changes. This is provided by deposited silica mechanical and/or physical protection of a biochemical response using a different metabolic pathway. The adequate amount of silica could also improve water balance,

plant growth and yield, rates of photosynthesis, reproduction and reduce grain chaff [162].

Crop plant productivity is critical for providing global food security. Relying only on natural plant growth for food commodity production is insufficient. Instead of additional macronutrients for plant growth, silicate fertilizer can also be applied to boost the productivity of many agricultural plants. Once agricultural productivity increases, the generation of residues also increases by enhancing extractable silica. Figure 5 illustrates the effect of two Si fertilizers on different crop plants. Crop production quantity enhancement ranges from 6 to 14%, 10 to 50% for blast furnace slag and potassium silicate, respectively. These positive responses are related to the fact that many crop plants such as rice, wheat, and sugarcane classified as highly Si-responsive plants with large Si demand [160]. The generation of extractable silica must be assumed as much as crop production to obtain a larger amount of silica from crop residues. For instance, Sun et al. [184] reported that silicon fertilizer application with maximum dosage in silicon-enriched soil increased the rice phytolith content by 32.83% in the stem, 27.01% in the sheath and 32.06% in the leaf.

Fig. 5 Crop residue enhancement generation using blast furnace slag and potassium silicate field fertilization [160]

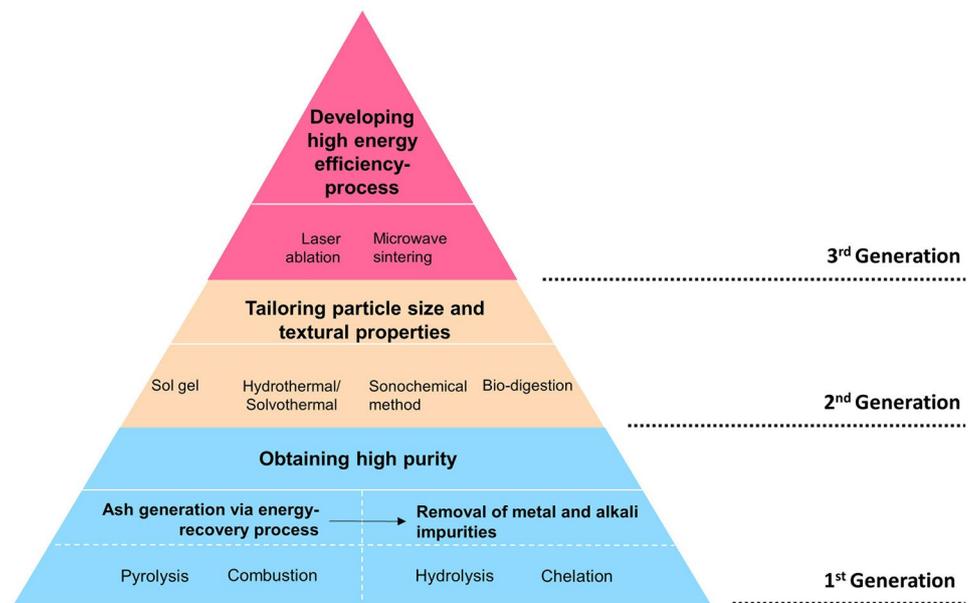


Preparation Methods for Silica Particles Derived from Crop Residues

The development of technological processes for extracting silica from crop residues can be classified into three levels regarding their conception and advancement as shown in Fig. 6. The modest silica recovery from crop residues should obtain high purity amorphous particles

by combining acid pre-treatment with a thermal process. Acid pre-treatment will remove the metal alkali impurities whereas organic fractions will be decomposed by thermal treatment. The next technology level focuses on tailoring the particle size, morphological, and textural properties of silica particles. Those technologies involve the sol gel method, hydrothermal/solvothermal, sonochemical method, and bio-digestion. The latest technologies exist

Fig. 6 Advancement of technological methods for silica extraction from crop residues



to answer the challenges for employing high energy efficiency and environmental-friendly methods to produce silica. In this case, laser ablation and microwave sintering are employed as efficient heat source to decompose organic compounds and control the textural and morphological properties of silica particles (Table 2).

Obtaining High Purity Amorphous Silica

Removing Organic Substances from Crop Residues

The destruction of the combustible portion in crop residues via thermal processing will be the simplest method to obtain silica. Numerous studies applied incineration, gasification, pyrolysis, or even modest combustion to generate amorphous silica from crop residues. In this method the operating temperature will be the major factor in generating targeted silica particles. Many studies employed thermal processing in temperature ranges of 500–900 °C to generate silica rich-ash. Instead of the effort to achieve high energy efficiency, lower operating temperature is applied to avoid the structural shifting of silica from amorphous into crystalline. In some cases, high alkali impurities in the ash will react with the silica to form ternary oxides which promote silica crystallization even at lower temperatures. For instance, crystalline phase silica was obtained using thermal processing at 650 °C for 3 h [92]. That was because of the high metal alkali impurities, up to 80 wt% in coconut husk ash, which had the high possibility to form ternary oxides promoting a crystalline structure. The thermal method will therefore be more suitable for

extracting amorphous silica from crop residues such as rice husk, rice straw, sugarcane leaf, teff straw, and wheat straw which have low metal alkali impurity content.

Removing Metal Alkali Impurities

Because numerous metal alkali impurities can be produced in ash from crop residues during the extraction process, many studies tried to modify the thermal process by employing acid or alkali pre-treatment to enhance the obtained silica concentration. Hydrolysis and chelation are two common mechanisms that can be employed in this acid treatment. Hydrolysis is frequently applied by utilizing concentrated acid [92, 94, 97, 102, 103, 110, 129, 151, 152] or alkali [92] to remove metal and alkali impurities in ash. On the other hand, chelation can eliminate metal alkali impurities by relying on the ability of carboxylic groups in milder acid [110, 144, 185] to chelate metal and alkali ion dissolved in solution.

Hydrolysis reaction

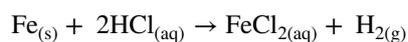
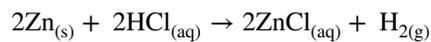
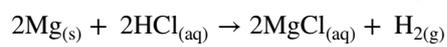
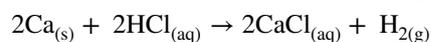
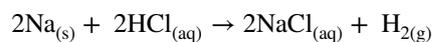
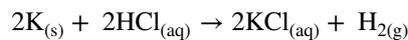
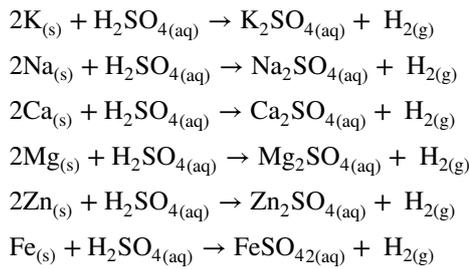


Table 2 Thermal process for silica extraction derived from crop residues

Raw material	Method	Operation condition	Silica purity, wt%	Major structure	References
Barley husk	Pyrolysis	650 °C, 8 h	85.00	Amorphous	[97]
Coconut husk	Combustion	650 °C, 3 h	11.65	Crystalline	[92]
Corn cob	Combustion	650 °C, 2 h	34.30	Amorphous	[108]
Corn stalk	Pyrolysis	620 °C	36.91	–	[98]
Oat straw	Combustion	1350 °C	31.40	–	[93]
Rice husk	Combustion	650 °C, 3 h	97.93	Amorphous	[101]
Rice husk	Combustion	600 °C, 2 h	95.77	Amorphous	[102]
Rice husk	Combustion	< 650 °C	91.48	Amorphous	[104]
Rice husk	Combustion	< 780 °C	91.48	Amorphous	[105]
Rice husk	Combustion	600 °C, 2 h	72.30	Amorphous	[107]
Rice husk	Combustion	600 °C, 4 h	95.60	Amorphous	[110]
Rice straw	Combustion	500 °C, 8 h	72.60	Amorphous	[95]
Sorghum bagasse	Combustion	800 °C	40.16	Amorphous	[99]
Sorghum husk	Combustion	800 °C	78.19	–	[100]
Sugarcane bagasse	Pyrolysis	1000 °C, 4 h	53.10	–	[103]
Sugarcane leaf	Combustion	650 °C	80.14	–	[96]
Teff straw	Combustion	900 °C, 2 h	91.81	Amorphous	[106]
Wheat straw	Combustion	500 °C, 8 h	88.09	Amorphous	[94]



Chelation reaction

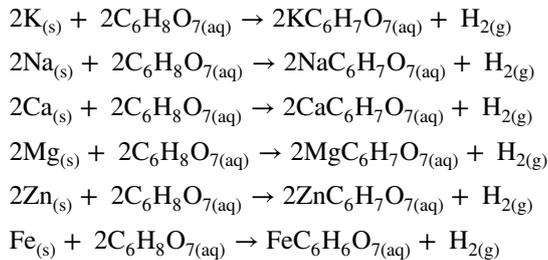


Figure 7 shows the highest silica purity and metal alkali removal efficiency that can be achieved by acid/alkali pre-treatment. The purity of silica particles derived from crop residues ranges from 88% up to nearly 100% [92, 97, 102, 103, 110, 151, 185] whereas the metal removal efficiencies are in the range of 70–96%. Higher acid concentration and longer reaction time is preferable

to extract silica from crop residues with relatively low silica content such as barley straw, coconut husk, and wheat straw [92, 94, 97]. It is beneficial to strongly reduce the higher metal alkali content in those crop residues.

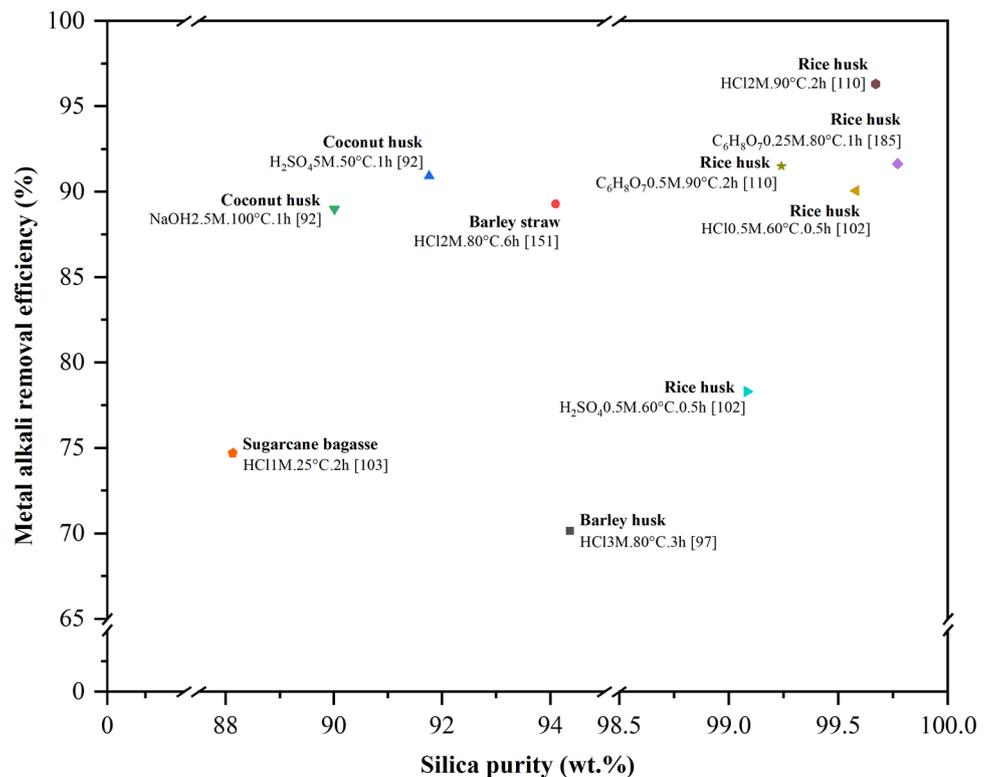
Chelation reactions using citric acid also exhibit relatively high removal efficiency for metal and alkali impurities (see Fig. 7), especially in crop residues with high silica content like rice husk. Umeda and Kondoh [185] obtained 99.77% silica purity and metal alkali impurities removal efficiency up to 92% using the chelation process using 5 wt% citric acid at 80 °C for 3 h. On the other hand, Azat et al. [110] applied the facile chelation method using rice husk dry mixing with 10 wt% citric acid to obtain 98.67 silica purity with 91.51% metal alkali removal efficiency.

Nano-Sized Silica Particles Derived from Crop Residues Textural Tailoring Properties

Hydrothermal/Solvothermal

Silica nano-particles with tunable textural properties can be generated from crop residues using hydrothermal [118, 119, 129, 139, 150] and solvothermal processes [128, 133]. These methods are such an advancement of acid hydrolysis which provide dual advantages in term of high purity and

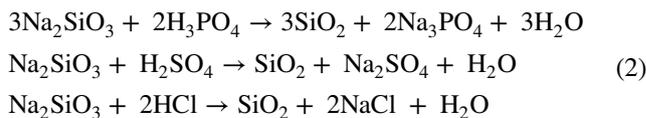
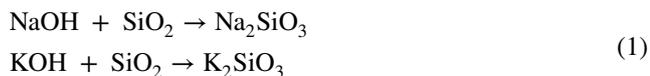
Fig. 7 Silica purity and metal alkali impurities removal efficiency obtained by acid pre-treatment



tunable particle size and morphology. In general, the solvothermal process produces similar results as the hydrothermal process, except that organic solvents are used instead of water to carry out the reaction. The utilization of high pressure is considerable to speed up the reaction among the reactants. Nano materials self-assembly in the solution is also obtained as a further stage in these methods [186]. As seen in Table 3, the hydrothermal process is carried out by employing organic acids such as citric acid, acetic acid, phosphoric acid, or hydrochloric acid to react with crop residues in a Teflon-lined autoclave under 120–150 °C temperature and 0.01–0.1 MPa pressure. The solvothermal method uses absolute ethanol as the reaction media to synthesize silica at 180–190 °C temperature and 0.1 MPa pressure. By increasing the temperature and pressure to its critical point, expected substances can be completely dissolved in the solvents [187]. In the final stage, the treated crop residues are dried and calcined at set temperatures to release water and solvents and remove organic compounds. The application of milder acids in hydrothermal method is strongly recommended to avoid hazardous residue and lower utilization of water during rinsing process.

Sol Gel Method

Sol gel method has been widely applied to generate silica particles from crop residues as seen in Table 4. It can be carried out through hydrolysis and polycondensation to obtain a sol/gel form of silica [188]. Fresh crop residues are often pre-treated using thermal [91, 106, 108, 121, 123, 124, 132], acid/alkali treatment [117, 127], or a combination of acid treatment and calcination [9, 99, 110, 122, 126, 130, 131, 134–136, 142] to eliminate unexpected impurities before being subjected to the sol gel method. Once the pre-treated crop residue is obtained, the sol gel process may begin as the following reactions:



Firstly, silica powder is subjected into alkali oxide solution like NaOH [9, 91, 99, 106, 108, 110, 117, 121, 122, 124, 126, 127, 130, 132, 134–136] or KOH [123, 142] to obtain a transparent silicate solution. Concentrated acids such as H₃PO₄ [117, 122], H₂SO₄ [121, 127, 130, 134], or HCl [9, 91, 99, 106, 108, 110, 123, 124, 126, 131, 132, 136, 142] are added drop wise to begin the hydrolysis process. Those acids cause the formation and condensation of ≡Si–OH which can form dimers dimmers or trimmers followed by their growth into particles [117]. Silica particle formation is frequently assisted by an aging process at room temperature for a set time [91, 99, 106, 108, 122, 130, 132, 134, 142]. In the final stage the sol/gel is dried and ground to obtain silica powder.

There are three types of final products that can be generated from crop residues through the sol gel method; uniform silica Nano-particles, silica xerogel, and silica aerogel (see Table 4). The pH value will be responsible to promote particle growth and spherical shape formation. Many studies used pH value in the 7–9 range to ensure silica particle formation (see Table 4). Zulfikar et al. [117] reported that silica suspension becomes very dilute at pH lower than 7 while silica particle agglomeration will be carried out at pH greater than 9. Dilute silica suspension can be directly precipitated to obtain high uniformity Nano-particles. Meanwhile, the agglomerated silica particles can form wet gel then generate silica xerogel and aerogel using a specific drying method.

Instead of pH adjustment, aging time and temperature must be utilized to achieve high colloid stability to promote the formation of Nano sized particles with a uniform size distribution. Le et al. [189] proved the aging temperature and time effects on silica Nano-particles stability in the presence of dispersing agents. As temperature increases from 30 to 60 °C, the interaction between the hydroxyl group on the silica surface with dispersing agent will increase which leads to generating better uniform distribution. At temperatures higher than 80 °C

Table 3 Silica extraction hydrothermal process

Raw material	Process condition	Final product	References
Rice husk	1 M HCl 120 °C, 0.1 MPa, 2 h	Silica nano-particles (10–30 nm)	[118, 119]
Rice husk	Ethanol 190 °C, 0.1 MPa 16 h	Porous silica	[128]
Rice husk	Ethanol 180 °C, 0.1 MPa, 24 h	Amorphous silica (101 m ² g ⁻¹ of specific surface area)	[133]
Rice husk	C ₆ H ₈ O ₇ 10% 150 °C, 0.01 MPa, 3 h	Silica nano-particles (249–250 nm)	[139]
Rice husk	CH ₃ COOH 10% 150 °C, 0.01 MPa, 3 h	Silica nano-particles (274–295 nm)	[139]
Rice husk	0.2 M H ₃ PO ₄ 150 °C, 0.01 MPa, 3 h	Silica nano-particles (239–242 nm)	[139]
Sorghum husk	1 M HCl 120 °C, 0.1 MPa, 2 h	Amorphous silica (spherical, saddle, and dumbbell shape)	[129]

Table 4 Sol gel method for synthesizing silica particles from crop residues

Raw material	Preliminary method	Silicate formation	Sol gel			Final product	References
			Sol/gel formation	Aging	Post treatment		
Corn cob	Calcination	1 N NaOH boiled 60 min	3 N HCl to pH 7	18 h 25 °C	Air drying at 80 °C for 24 h	Silica nanoparticle	[91]
Corn cob	Calcination	3 N NaOH 70 °C 4 h	3 N HCl to pH 7	18 h 25 °C	Air drying at 75 °C for 24 h	Silica nanoparticle	[108]
Corn cob	Calcination	1 N NaOH boiled 3 h	1 N H ₂ SO ₄ to pH 7 and 10	–	Air drying at 80 °C for 24 h	Silica nanoparticle	[121]
Corn stalk	Acid leaching, calcination	3 M NaOH refluxed 5 h	3 M HCl till gelation	50 °C with 3 different solvents	Air drying at 50 °C for 24 h	Silica xerogel	[126]
Rice husk	Acid leaching, calcination	2 M NaOH 90 °C 2 h	2 M HCl till gelation, neutralized by hot water	–	Air drying at 105 °C for 4 h	Silica xerogel	[110]
Rice husk	Acid leaching	10 wt% NaOH 90 °C 1 h	3 M H ₃ PO ₄ to pH 7–9	–	Freeze drying, calcination	Silica xerogel	[117]
Rice husk	Calcination	1 N NaOH 90 °C 2 h	1 N HCl to pH 2–3; kerosene + dual surfactant; NH ₄ OH to pH 7	1 h at 25 °C	Supercritical CO ₂ drying at 150 bar 50 °C for 8 h	Silica aerogel	[120]
Rice husk	Acid leaching, calcination	2 M NaOH 90 °C 2 h	85% H ₃ PO ₄ to pH 7 in the presence of ethanol	30 min 25 °C and 65 °C	Hot water washing, calcination	Silica nanoparticle	[122]
Rice husk	Calcination	1.5 M NaOH 100 °C 1 h	1 M HCl to pH 7	50 °C 12 h	Air drying at 80 °C for 48 h	Silica xerogel	[124]
Rice husk	Calcination	1 M NaOH 100 °C 3.5 h	1 M NH ₃ to pH 4–6	–	Ambient pressure drying at 60 °C for 2 h	Silica aerogel	[125]
Rice husk	Acid leaching, calcination	4 M NaOH 80 °C 4 h	5 M H ₂ SO ₄ to pH 9	30 min at 25 °C	Air drying at 80 °C for 24 h	Silica xerogel	[130]
Rice husk	Acid leaching, calcination	1.5 M NaOH 90 °C 1 h	1 M HCl to pH 4	70 °C 7 days	Air drying at 70 °C for 48 h	Silica nanoparticle	[131]
Rice husk	Calcination	1 M NaOH 90 °C 2 h	1.5 M HCl to pH 1	24 h 25 °C	Air drying	Silica aerogel	[132]
Rice husk	Acid leaching, calcination	0.1 M NaOH	NH ₄ OH to turbid color	–	Air drying at 80 °C for 24 h	Silica nanoparticle	[135]
Rice straw	Acid leaching	NaOH (2.0%, w/v) 100 °C 3 h	1.5% (v/v) H ₂ SO ₄ to pH 6.5	–	Air drying	Silica nanoparticle	[127]
Sugarcane bagasse	Calcination	2 M NaOH 90 °C 1 h	1 N HCl to pH 7–10	10–48 h at 25 °C	Vacuum drying at 80 °C for 12 h	Silica xerogel	[116]
Teff straw	Calcination	2.5 N NaOH 85 °C 1 h	HCl to pH 10–13.4	20 h at 25 °C	Air drying at 60 °C for 24 h	Silica xerogel	[106]

however, adsorbed dispersing agent molecules in the silica hydroxyl group will be desorbed, exposing a reverse effect on the particle size distribution. The increase in aging time may narrow the particle size distribution but note that the set time must be able to achieve dissolution equilibrium ensuring better silica particle distribution in the solvents.

Xerogel and aerogel are two silica states resulting from the sol gel method can be affected by the drying process as seen in Fig. 8. Xerogels refer to a solid formed by evaporative gel drying with unhindered shrinkage [186]. Once supercritical drying is applied to remove solvents, that solid is called as aerogel. In general, silica xerogel exhibits a lower specific surface area compared with that

of silica aerogel as seen in Fig. 9. Those silica xerogels possess 100–400 m²/g of specific surface area and 2–25 nm of average pore diameter [110, 116, 117, 124, 126, 130]. It is related to the fact that the liquid gel phase will be removed during evaporative drying, promoting extreme shrinkage greater than 90% on silica particles. In contrast, less shrinkage will be observed during supercritical drying affected by retaining a solid network through liquid gel-gas replacement. Thus, large specific surface area can be obtained with silica aerogel. Rajanna et al. [120] reported that granular silica aerogel from rice husks poses 637.6 m² g⁻¹ specific surface area, 1.2 cm³ g⁻¹ pore volume, and 6.6 nm pore diameter. Abbas et al. [132] also investigated silica aerogel properties derived from rice husk which are slightly different. That silica aerogel exhibits 769 m² g⁻¹ specific surface area, 2.81 cm³ g⁻¹ pore volume, and 13.2 nm pore diameter. Other silica xerogels derived from rice husk were successfully obtained by Feng et al. [125], showing 945.8 m² g⁻¹ specific surface area, 0.899 cm³ g⁻¹ pore volume, and 3.80 nm pore diameter.

Sonochemical Method

Further processing methods are being required during silica synthesis to obtain silica Nano-particles microstructural size and surface-to-volume ratio. The sonochemical method presents an emerged technique to generate those required properties. High intensity ultrasound is utilized to create acoustic cavitation which generates high temperatures and high pressure at the center of the exposed area [186]. Those conditions produce hydrogen and hydroxyl radicals in aqueous solution which are then diffused into liquid, increasing the nucleation and growth rate with better size distribution.

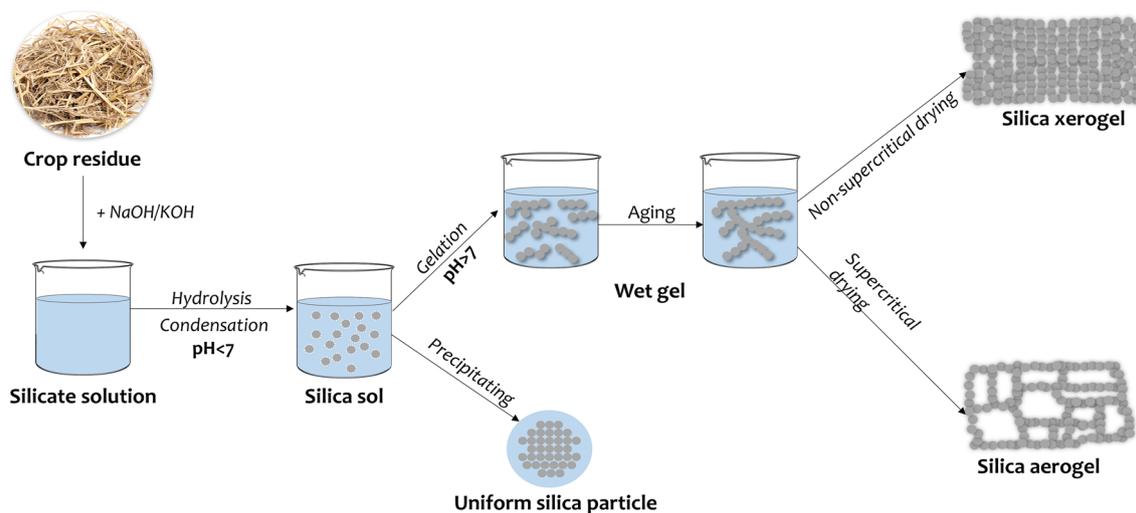


Fig. 8 The silica synthesis process via the sol gel method derived from crop residues

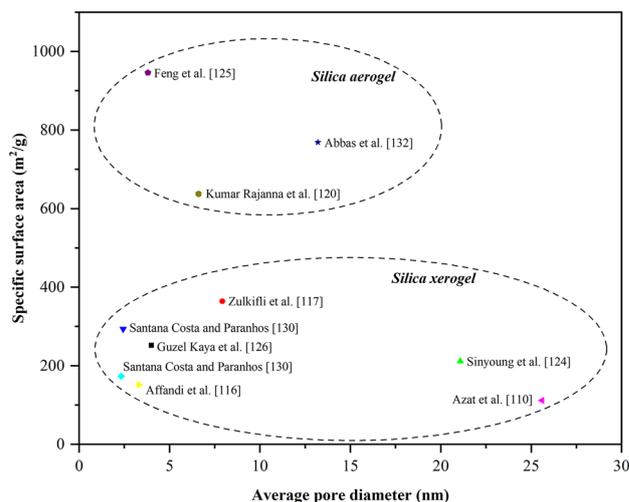


Fig. 9 Silica xerogel and aerogel textural properties derived from crop residues

In the sol gel process, those radicals are produced in the hydrolysis stage which enhance condensation and decrease the overall reaction time.

In silica synthesis using crop residues, the sonochemical method assists the acid leaching and combustion process [115]. The sol-gel method [112], produces size-controllable Nano-particles. Salavati-Niasari and Javidi [112] utilized high-intensity ultrasound (600 W at 20 kHz) to synthesize silica Nano-particles from rice husk. Their study implied that controllable silica particle size can be achieved at 10–30 min sonication. Longer sonication time will promote Nano-particle agglomeration caused by high pressure shock waves, micro-emission fluid and the Nano-particle “Brown phenomenon”. Sankar et al. [115] investigated the sonication

time effect on silica Nano-particle textural properties derived from rice husk. They used lower power (240 W) and higher frequency (35 kHz) during sonochemical reaction. Regarding their study, longer sonication time beyond 50 min will be capable of enhancing silica Nano-particle porosity. Specifically, the synthesized silica Nano-particles possess 271.22 $\text{m}^2 \text{g}^{-1}$ specific surface area, 0.306 $\text{cm}^3 \text{g}^{-1}$ pore volume, and 4.11 nm average pore size.

Bio-Digestion Method

The bio-digestion process for extracting silica from crop residues is identical to the sonochemical method in term of controlling the silica particle Nano size. Bio-digestion relies on the organism's ability [137, 138] or even microorganisms [95] to degrade organic matter via enzymatic hydrolysis and generate silica Nano-particles through mechanical works produced by their digestion organs. Further processes such as calcination and acid leaching are required after bio-digestion to remove organic matter and metal alkali impurities from the resulting humus. Torres et al. [138] argued that vermicomposting techniques are preferable to achieve specified silica particle crystal arrangement. This is related to the different size and shape of phytolith as the resulting diverse chemical structure present in plants such as proteins, lignin and polysaccharides. Red wiggler worms are preferable in vermicomposting to obtain silica particles from crop residue due to their unique characteristics. These worms eat their weight daily, excrete 60% of the ingested plant material as humus, show prolific profile, poses longer life time up to 16 years, resist aggressive environments, and can digest crop residues that contain high concentrations of silica [137, 138]. Esteves et al. [137] used a wood container (45 × 30 × 22 cm) with 5000 red worms to produce humus from rice husk for 1 month. That process can achieve 88% production

efficiency with 55–250 nm of silica particles. Another study conducted by Torres et al. [138] employed a small-scale system made of hemlock wood (50 × 35 × 25 cm) with 1000 red worms to generate silica Nano-particles from nixtamalized corn with two month processing. This experimental setup can achieve 90.21% of production efficiency which means higher than a previous study. Moreover, the resulting silica particle exhibits a hemispherical shape with 100 nm. size. Further analysis reported that it can be defined as mesoporous silica with 9.1 $\text{cm}^2 \text{g}^{-1}$ specific surface area, 0.027 $\text{cm}^3 \text{g}^{-1}$ pore volume, 18.4 % porosity, and 11.99 average pore diameter.

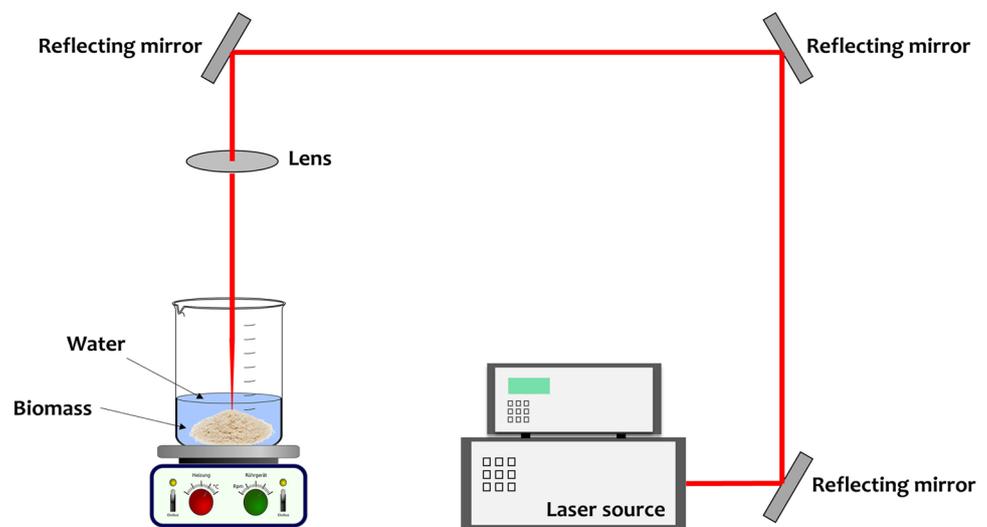
Method for Achieving High Energy Efficiency and Low Environmental Impact

Laser Ablation

Pulsed-laser ablation is expected to replace the conventional method to synthesize silica particles with controllable textural properties. Figure 10 illustrates laser ablation process for silica extraction from crop residues. In principle, pulse energy radiation can be utilized to damage biomass fibrous structure or even unexpected metal alkali impurities to obtain silica. The destruction of unwanted compounds can be obtained by adjusting several parameters such as the wavelength, pulse duration, and pulse repetition rate to generate the appropriate pulse energy. By understanding the required energy to break down certain impurities in crop residues, it is possible to produce high purity silica.

San et al. [114] utilized this method to synthesize silica Nano-particles from sugar beet bagasse. Silica Nano-particles were achieved by employing 16 mJ of pulse energy to remove organic compounds from sugar beet bagasse. That energy is achieved by conducting a commercial Nano

Fig. 10 Laser ablation process for silica extraction from crop residues, adapted from Rawat et al. [190]



second pulsed Neodymium-doped Yttrium Lithium Fluoride (Nd:YLF) laser operating at 527 nm with a pulse duration of 100 ns and an average output power of 16 W at a pulse repetition rate of 1 kHz. The silica particles produced by that laser ablation method are in the 38–190 nm size range with an average size of ~ 74 nm.

Microwave Sintering

Microwave sintering is well known as the most popular energy source to heat dielectric materials in industrial applications with high processing time efficiency and energy consumption [111]. Microwaves are electromagnetic energy in the 300 MHz to 300 GHz frequency range [186]. That heat energy is useful for transforming amorphous silica into its crystalline phase [111] or assisting the sol gel method to promote nucleation and Nano-particle growth [113].

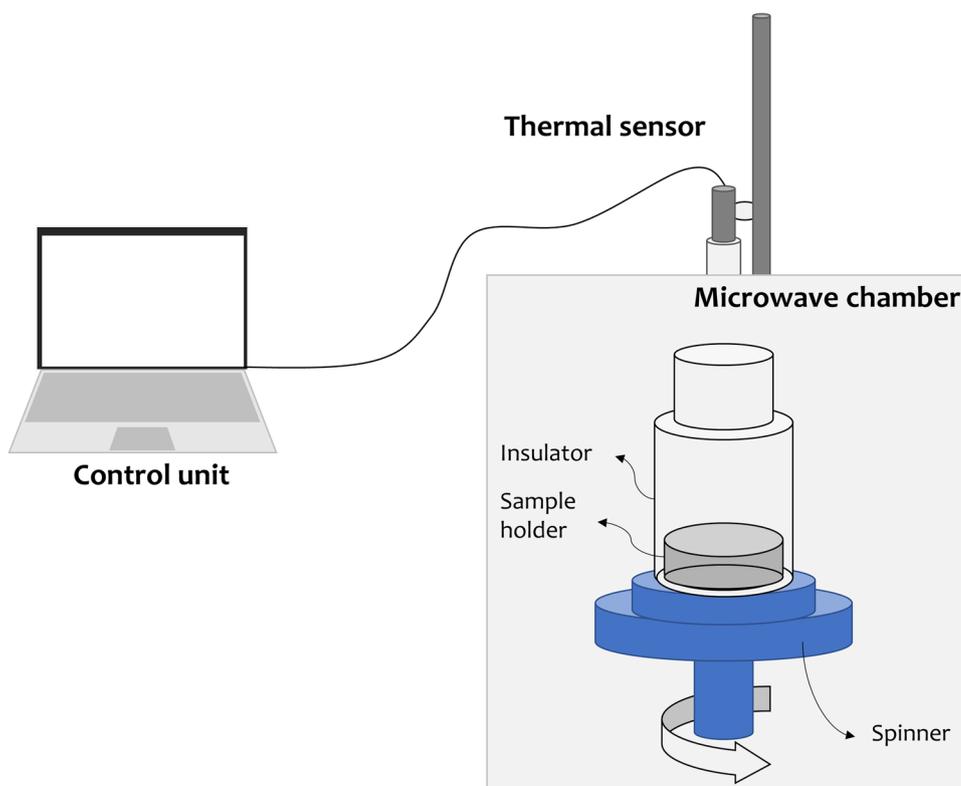
Makul et al. [111] investigated silica particle properties prepared from rice husk ash using rapid 2.45 GHz microwave sintering at 800–1200 °C temperature range (see Fig. 11). The resulting silica particles are observed as SiO_2 -cristobalite with some α - SiO_2 . Increasing the temperature up to 1100 °C will completely remove the silica amorphous phase. Another study by Pijarn et al. [113] used microwave radiation at 300 W for 60 min to assist the sol gel method in producing silica gel from rice husk. Silica gel produced using this method exhibits 50–70 nm particle size,

10–30 nm pore size diameter, 0.7 – $1.0 \text{ cm}^3 \text{ g}^{-1}$ pore volume, and 400 – $700 \text{ m}^2 \text{ g}^{-1}$. These textural properties are not significantly different from the commercial silica gel tested in that study.

Preferable Routes for Preparing Silica Particles Derived from Crop Residues

Selecting routes for generating silica particles from crop residues not only regards on the desired properties of final product, but also the energy efficiency, operation time, and environmental impacts. Figure 12 illustrate the routing process for obtaining a preferable method of silica preparation from crop residues. Although showing shorter operation time and ease of operation, thermal methods are reasonably avoidable due to the utilization of high operation temperature. High generation of acid residues become a major barrier for the application of acid leaching for preparing silica from crop residues. The improvement by altering strong acid with carboxylic acid is not sufficient to generate tunable properties of silica particles. Biological processes by utilizing the digestion of red worm provide an interesting alternative for generating silica Nano-particles from crop residues. However, those exhibit longer operation time, worsen by additional acid leaching which can generate dangerous acid residues. Laser ablation becomes a promising technological method for preparing silica nano-particles with controllable

Fig. 11 Microwave sintering for silica extraction from crop residues, adapted from Makul et al. [111]



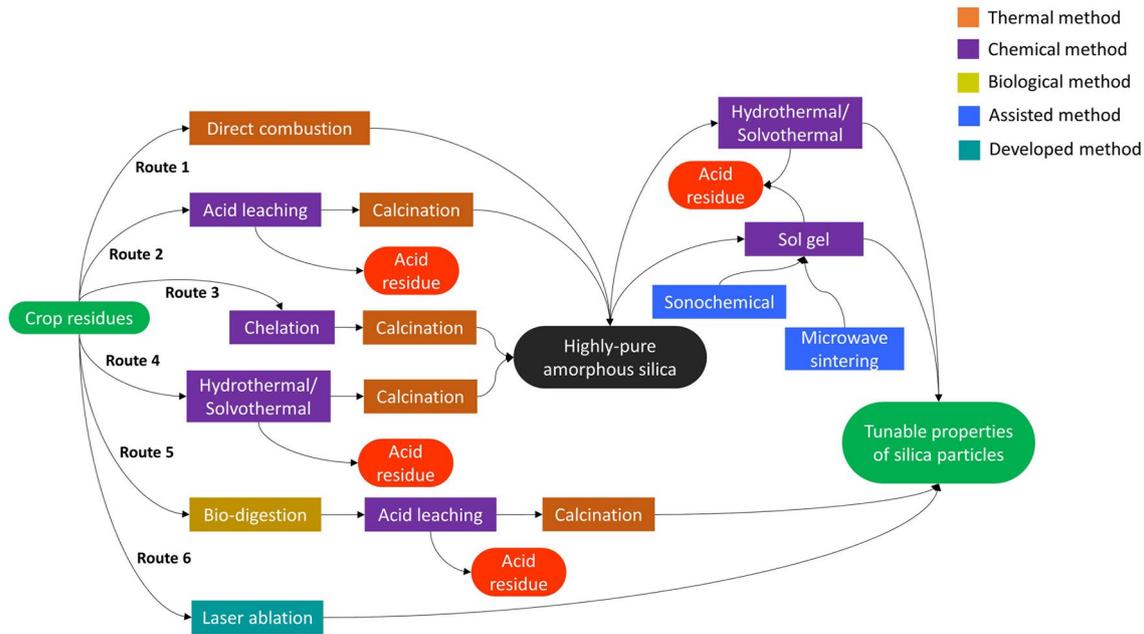


Fig. 12 Routing of preferable method for preparing silica particles from crop residues

properties. It provides several advantages regarding operation time and processability.

Recent Progress on Silica Material Applications Derived from Crop Residues

The typical properties of silica particles will determine compatibility in certain application fields. Figure 13 shows the correlation between the synthesis method, achieved properties, and silica particle applications derived from crop residues. Amorphous silica particles prepared using thermal methods are frequently applied in the fabrication of concrete and ceramics. By enhancing their purity, it will be possible to apply them in preparing valuable materials such as high-quality concrete, adsorbent, composites, membranes, ER fluids, and mesoporous material precursors. Additionally, pure silica Nano-particles are required in biomedical applications, thermal insulation purposes, catalyst fabrication, and chromatography stationary phases.

Concrete Materials

Many studies investigated concrete mechanical performance improvement by the presence of amorphous silica particles derived from crop residues as partial replacement for ordinary concrete materials. Carreno et al. [101] reported that compressive strength values of $755.06 \text{ kg f cm}^{-2}$ can be obtained at 28 days by replacing 40% of cement with

micro-milled RHA material treated at 650°C . Another study conducted by Amin et al. [109] reported that significant improvement in strength, stiffness, toughness, and ductility can be observed in concrete containing 15 wt% wheat straw ash at 91 days. Crop residue ash can also mix with other materials to partially replace cement in concrete fabrication. Pandey and Kumar [173] mixed rice straw silica along with commercial micro-silica as partial replacement for Ordinary Portland Cement (OPC) to improve the mechanical strength of Pavement Quality Concrete (PQC). Maximum compressive, flexural and tensile strength are found when OPC was partially replaced by 5%–7.5% rice straw silica and micro-silica composite. Sorghum husk ash was mixed with Laterite to partially replace Ordinary Portland Cement (OPC) up to 20% in concrete construction [191]. Unfortunately, the compressive strength is insufficiently improved at early curing time.

A distinct role is taken by silica particles derived from crop residues in concrete development. Sinyoung et al. [124] utilized silica Nano-particles derived from rice husk ash to synthesize belite cement by firing with two different calcium sources (calcium carbonate and calcium nitrate). That silica Nano-particle is sufficiently reactive to form the principal phase in belite cement (larnite or $\text{b-C}_2\text{S}$) at temperatures of 800°C , especially with calcium nitrate as the calcium source. On the other hand, Junaidi et al. [144] successfully synthesized a super hydrophobic coating from rice husk ash via mechanochemical modification and spray coating. Although the coated concrete shows high contact angle up to 157.7°C , it requires considerable further improvement

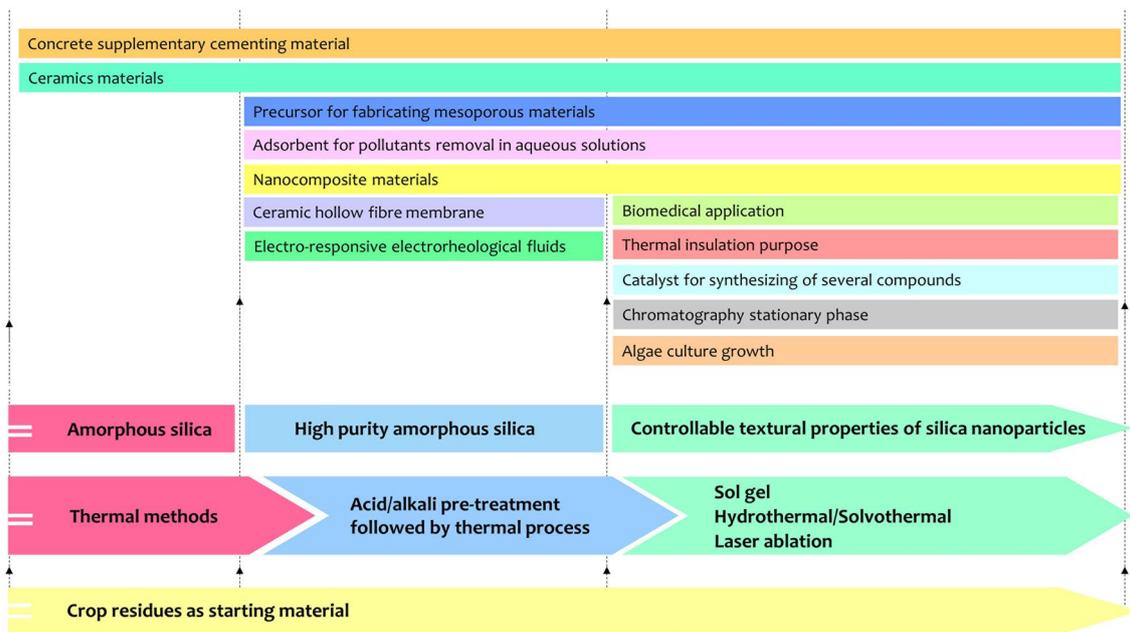


Fig. 13 Various silica applications based on their preparation methods and characteristics

to enhance its practical use in construction and building applications.

Refractory Ceramic Materials

Silica particles derived from crop residues were certainly observed to present an amorphous structure. The crystallization process at temperatures higher than its melting point can generate a silica crystal phase like quartz, cristobalite, tridymite, etc. Fernandes et al. [192] reported that thermal treatment at 1000 °C will be affordable to obtain silica with cristobalite and tridymite crystalline phases. These silica crystals are beneficial components for preparing refractory ceramics. Furthermore, silica particles can also be incorporated with other ceramic reinforcement materials in different aluminum matrix forms to achieve good strength and ductility combinations [145].

Several studies were carried out to investigate the possibility of using silica derived from crop residues in fabricating refractory ceramics by replacing kaolin clay. Sobrosa et al. [104] developed refractory ceramic materials by replacing kaolin clay with rice husk silica at different volume percentages. The use of 10% silica resulted in increased mechanical strength without decreasing the thermal shock strength. The rice husk silica effect on the mechanical and thermal properties of refractory ceramic materials was also investigated by Stochero et al. [105]. Refractory ceramics are fabricated by replacing kaolin clay with 20% rice husk silica and different volume percentages of steel fibers. The results imply that significant improvement in the mechanical and

thermal properties of refractory ceramics can be obtained by replacing kaolin clay with rice husk silica and steel fibers. Other studies were conducted to fabricate glass–ceramic tiles using rice husk as silica precursors. Glass–ceramic tiles were successfully developed by Andreola et al. [193] using a sinter-crystallization process at 900 °C using a glassy frit formulated in the MgO–Al₂O₃–SiO₂ composition system. Those ceramic materials exhibited higher bending strength and Mohs hardness compared with commercial glass–ceramics.

Thermal Insulation Purposes

The extracted silica particles from crop residue can be derived into refractory materials that have enhanced thermal and acoustic insulation performance. Amorphous rice husk silica has been investigated for forsterite refractory and refractory cordierite preparation, which have beneficial characteristics as thermal insulators. Hossain et al. [194] investigated the amorphous rice husk silica effect on the phase formation and physical characteristics of forsterite refractory materials prepared from quartz and MgO powder at 1100 °C sintering temperature. Better reaction between amorphous silica and periclase, which promotes forsterite phase formation, will be increased at higher rice husk silica loads. The presence of forsterite phase results in decreased density, porosity, and thermal conductivity, which are affordable for thermal insulation purposes. Another study by Sembiring et al. [142] prepared refractory cordierite from rice husk silica, Al₂O₃, and MgO powders at the sintering temperature

range of 1050–1035 °C. At that temperature range the spinel and cristobalite from the raw materials transform into cordierite followed by a decrease in the density, porosity, and thermal expansion coefficient.

A new thermal and acoustic insulation material was successfully prepared from corn stalk silica [126]. Silica xerogel is first synthesized from corn stalk ash in ambient pressure drying using the sol gel method. This silica xerogel is then used to fabricate silica xerogel/epoxy Nano composites. Higher amounts of silica xerogel in the epoxy resin enhance thermal stability and reduce the Nano-composite epoxy thermal conductivity. The presence of 1.5 wt% silica xerogel will decrease the acoustic velocity from 2541 m/s to 2373 m/s. A slight increase in Nano composite epoxy water sorption will be obtained with the addition of silica xerogel. These Nano composite epoxy characteristics will be suitable for thermal and acoustic insulation purposes.

Adsorbent for Pollutant Removal in Aqueous Solutions

Gadolinium (Gd (III)), mercury (Hg (II)), lead (Pb (II)), and ciprofloxacin drugs are pollutants in aqueous solutions that can be managed using silica materials derived from crop residues. Silica powder and silica gel derived from rice husk ash are successfully utilized to prepare polymers and grafted copolymers for the adsorption of gadolinium [123]. This result indicates that silica gel grafted copolymer possesses maximum Gd (III) adsorption capacity of 229.36 mg g⁻¹ which is higher than the other adsorbent used in Gd (III) adsorption in other works. The Hg(II) adsorption process can be carried out using NaA zeolite derived from barley husk ash [97]. That zeolite material will be a promising adsorbent for Hg²⁺ ions removal from aqueous solutions indicated by high adsorption efficiency as great as 98%. Another study by Hassan et al. [195] prepared low-cost fibrous silica KCC-1 derived from rice husk ash for Pb(II) removal. The adsorption–desorption analysis implies that KCC-1 (RHA) is affordable as a good adsorbent for eliminating Pb (II) from aqueous solutions. This is indicated by good adsorption–desorption for five cycles with a reduction in Pb (II) removal percentage from 75 to 43%, and 65% to 27%. In addition, the silica Nano structure derived from rice husk has good adsorption capacity for ciprofloxacin drug removal from aqueous media [134]. That silica Nano-particles show maximum ciprofloxacin adsorption capacity at 190 mg/g is much higher than that of commercial silica gel (11.0 mg/g) under the same optimum conditions.

Biomedical Application

The application of silica particles derived from crop residues on biomedical is strongly dependent upon their compatibility

with human mesenchyme stem cells [118, 119, 129]. Biocompatibility assessment was conducted by Alshatwi et al. [118] and Athinarayanan et al. [119] to determine the biogenic silica Nano-particle potential derived from rice husk in biomedical applications. Those studies reported that biogenic silica Nano-particles prepared from rice husk are applicable in bone tissue engineering due to their excellent compatibility toward human mesenchyme stem cells. Periasamy et al. [129] tried to investigate the biocompatibility of silica nano-particle derived from sorghum husk crop residue. The silica particles harvested from sorghum husk is an amorphous solid with spherical, dumbbell, saddle, and sinuous shaped particles 10–200 µm in size. It is also claimed as nontoxic material with excellent biocompatibility with human mesenchyme stem cells with high potential for tissue engineering in biomedical fields.

Other silica biomedical applications were studied by Rajanna et al. [120] and Prabha et al. [135]. Hollow silica aerogel microspheres derived from rice husk are useful as drug delivery vehicles, indicated by fast release of ibuprofen from silica particle load compared to pure crystalline ibuprofen and other loaded forms [120]. On the other hand, a UV–Vis spectroscopy analysis indicated that silica Nano-particles derived from rice husk are useful for bio imaging applications indicated by photoluminescence emissions in the visible region. Hence, it is possible to utilize that material for theranostic applications by good drug conjugation arrangement on the Nano-particle surface [135].

Catalyst Applications

The application of silica particles derived from crop residues in catalyst synthesis generate valuable compounds have been widely investigated. Salakhum et al. [108] prepared hierarchical faujasite Nano sheets using corn cob ash-derived Nano silica in the presence of a hierarchical porogen. The obtained materials show outstanding catalytic properties for the hydrogenation of lignin-derived alkylphenols. Another study by Davarpanah et al. [147] synthesized Nano acid catalyst derived from rice husk silica for the synthesis of 3,4-Dihydropyrimidinones/thiones compounds. This Nano catalyst shows several advantages related to excellent targeted product yields in a short period of time and recovery process flexibility. In addition, rice husk silica can also be applied to homemade biocatalyst preparation via lipase physical adsorption for optimizing cosmetic ester enzymatic synthesis [128]. That homemade biocatalyst exposes high catalytic activity in solvent and solvent-free systems and operational stability with potential for further applications in industrial scale cosmetic ester synthesis.

Rice husk silica can also be employed as supporting materials for iron catalysts to conduct heterogenous fenton degradation for oxalic acid [143] and organic dyes [136].

The great catalytic activity of those materials is related to the silica mesoporous structure which provides sufficient cavities and surface area, creating more active sites for targeted compounds. The distinct dye degradation mechanism was carried out using carbon-containing SiO₂-based photo catalysts prepared from husks-derived biogenic silica using the solvothermal method. Rice husk silica-derived catalysts exhibit higher adsorption capacity, indicating that RhB adsorption is carried out through a basic mechanism via interactions between hydroxyl groups in the SiO₂ surface with the cationic species on dye compounds [133]. A similar adsorption mechanism was also obtained by Velmurugan et al. [91] when amorphous silica from corn cobs were utilized to adsorb methylene blue. In that process, extracted silica acts as an electron transfer mediator between the silica particles and methylene blue by acting as a redox catalyst.

Other Valuable Applications

Shahnani et al. [159] utilized silica derived from rice husk for the chromatography stationary phase. Microsphere silica is prepared using the sol gel method in the presence of nonionic surfactant, P123. The prepared silica microsphere is then packed with an analytical column to evaluate 10-deacetylbaocatin III and rutin separation from taxol and hesperidin, respectively. The HPLC chromatograms of those two mixtures exhibit acceptable resolutions among the analytes. This advantageous result implies that spherical and porous silica particles from rice husk are promising for development of liquid chromatography stationary phase. Rice husk-based silica Nano particles have also been applied in electro-responsive electro rheological (ER) fluids fabrication. Kwon et al. [152] investigated the ER properties of a rice husk-based Nano-silica suspension using a rotation rheometer under various electric field strengths. The Nano silica particles exhibit excellent ER performance indicated by higher storage moduli and shear relaxation modulus property. Therefore, those silica Nano-particles can be considered as a promising ER fluid component.

Challenges and Future Works in Developing Silica Materials from Crop Residues

Silica Depletion in Soil Due to Crop Residues Utilization

Phytolith is a typical term that specifies deposited amorphous silica in intracellular or extracellular plant compartments. It is known as a major component of biogenic silica along with zoogenic, protistic, and microbial silica components in soil [196]. As shown in Fig. 14, phytolith

is involved in the biogeochemical silica cycle in croplands and considered as the most important source of soluble silica on a biological time scale due to its higher solubility and cycling process. However, crop residues containing high phytolith concentrations will be removed from crop lands during the harvesting process. The removal of phytolith from crop lands will interfere with the biogeochemical silicon cycle in croplands by interrupting silicic acid replenishment in soil. This condition provokes routine silicate fertilizer application to heal the silica availability in soil. It may increase the production cost but sometimes retain the soil pollution produced by chemical fertilizer.

Silica depletion in croplands has become a critical issue for synthesizing silica from crop residues into various siliceous products. The development of Si fertilizer from other sustainable sources has become a decent option to overcome this dilemmatic condition. Many studies have investigated various industrial wastes as Si fertilizer for crop plants. Haynes et al. [198] evaluated four kinds of industrial wastes (blast furnace slag, steel slag, processing mud, fly ash) as sources of silicon fertilizer for paddy rice plants. The results reported that all materials except fly ash enhanced the amount of extractable silica in soil. It was furthermore confirmed that blast furnace slags were the most effective waste materials as fertilizer-Si sources among the tested waste materials. Other industrial wastes with high silica content such as sewage sludge [199], waste silicon sludge [200], silicon kerf waste [201], waste products from the phosphate fertilizer industry [202] may also be considered as fertilizer-Si sources.

Segregated Approach to Valuable Components Recovery from Crop Residues

Various silica materials with compatible properties were synthesized from crop residues using numerous methods. Those methods involve a segregated approach to recover valuable compounds from crop residues. During silica extraction, organic compounds and metal alkali impurities as unwanted matter are removed and thrown away without further processing. Therefore, it is preferable to conduct an integrated technological method to completely recover valuable components from crop residues. Several studies were carried out to synthesize silica along with a conversion process toward crop residue organic compounds. Zhang et al. [46] consecutively prepared d-xylose and pure superfine silica from rice husk. Similarly, Barana et al. [53] and Krishania et al. [47] employed the same idea to prepare silica along with lignocellulosic material from rice husk and rice straw, respectively. Further investigation by Zhang et al. [7] improved their previous study to obtain d-xylose, organosolv lignin, ethanol and amorphous

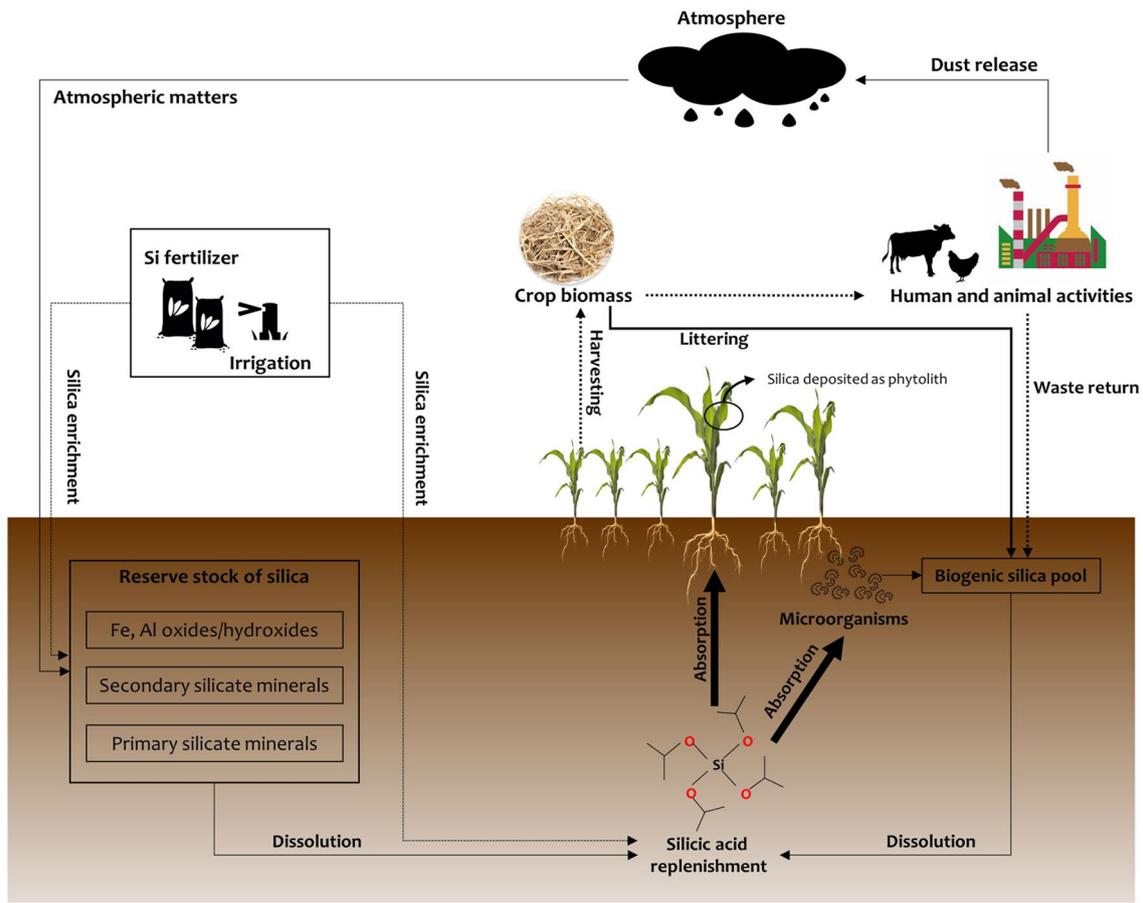


Fig. 14 Biogeochemical silica cycle in croplands [197]. Solid lines represent natural processes while dotted lines represent processes controlled by human activities

superfine silica, simultaneously. Another study by An et al. [203] and Liu et al. [30] synthesized activated carbon from rice husk ash along with silica extraction. In addition, auto thermal fluidized rice husk bed gasification was conducted by Thakkar et al. [9] to extract silica and energy, consecutively. A schematic illustration of simultaneous recovery of valuable materials from crop residues is provided in Fig. 15.

Development of Green Technology for Recovering Silica from Crop Residues

Most of the methods mentioned in this study utilize a high temperature process to remove the major constituents from crop residues. Concentrated acids such as HCl, H₂SO₄, H₃PO₄ are used in the silica extraction process to remove metal alkali impurities. Alkali oxides such as NaOH and KOH are also used to obtain silicate components such as silica precursors with the sol gel method.

The utilization of chemical reagents may generate hazardous liquid residues which are harmful for biotic components. This problem can be solved by employing an integrated process using green reagents and novel high efficiency heat sources. Milder acids such as citric acid [110, 139, 144, 185] and acetic acid [139] can be applied via the chelation process to remove metal alkali and avoid dangerous residues. Laser ablation [114] and bio-digestion [137, 138] are two techniques that can decompose organic compounds and generate Nano-sized particles from crop residues. A schematic of the proposed green technologies for silica recovery from crop residues is shown in Fig. 16.

Novel Application Of Silica Materials Derived From Crop Residues

Silica is well-known as an inorganic filler that has been received more attention for mixed matrix membranes

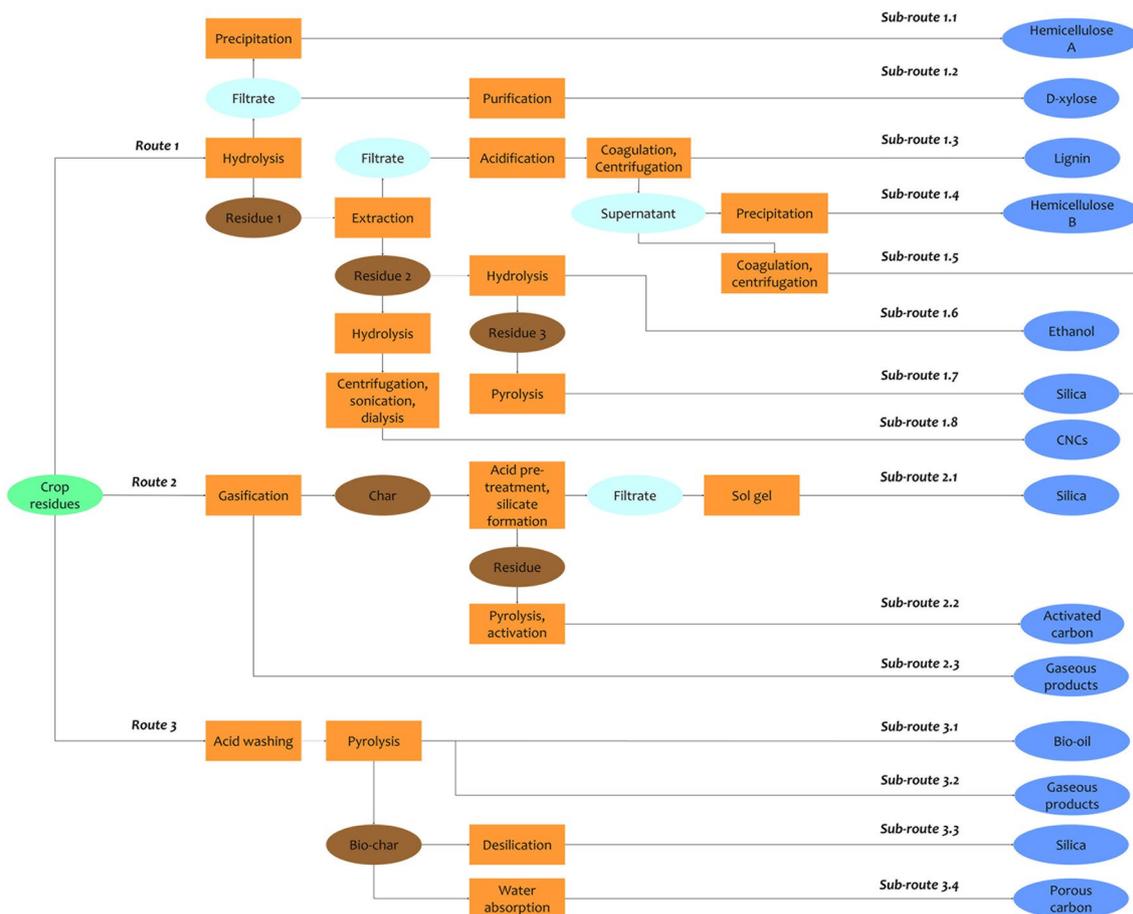
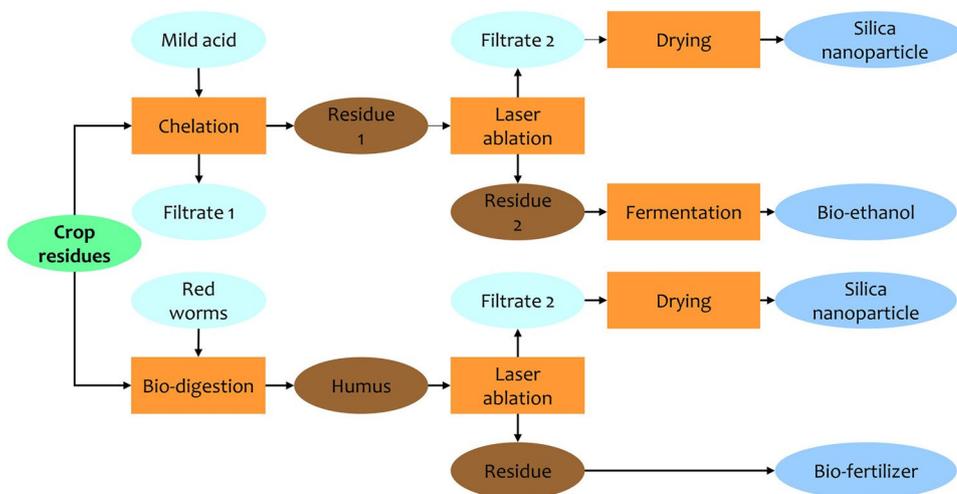


Fig. 15 Simultaneous recovery of valuable components from crop residues, adapted from Zhang et al. [7], and Su et al. [29], Barana et al. [53], Kauldhar et al. [127], and An et al. [203]

(MMMs) development, especially for gas separation process. MMMs are fabricated by combining polymer as the continuous phase and inorganic material as the dispersed phase. Silica particles are expected to rearrange the chain packing

of polymer matrix, providing desired diffusional gas pathway. Recently, most of applied silica on MMMs are commercial products [204–208] or synthesized by chemical precursors such as tetraethyl orthosilicate [209–212], tetramethyl

Fig. 16 The proposed green technologies for recovering silica from crop residues, adapted from San et al. [114], Esteves et al. [137], and Torres et al. [138]



orthosilicate [213], sodium metasilicate [214]. Besides, there are only few studies synthesizing silica particle from crop residues such as rice husk and rice straw. Waheed et al. [215] synthesized mesoporous silica particles from rice husk ash through sol gel method, then applied as inorganic fillers in polysulfone based MMMs. The mesopore structure of rice husk silica was observed to be beneficial to create faster diffusion of the penetrant gases. Likewise, Bhattacharya and Mandal [216] utilized silica Nano-particles derived from rice straw as filler to synthesize nano-composite polymeric membrane comprising polyether-polyamide block co-polymer (PEBA). A substantial improvement on CO₂ permeability was observed after silica loading into PEBA matrix. By considering these two studies, development of silica materials from crop residues can be considered as good alternatives for inorganic fillers for preparing MMMs.

Conclusion

The following summary and conclusion can be stated from this review:

1. The crop residues as affordable silica precursors are strongly associated with their high silica ratio, global productivity, and the silicate fertilizer effect for improving crop production.
2. The silica extraction method from crop residues can be classified into three levels: (1) obtaining high purity amorphous silica, (2) tailoring the morphological and textural properties of silica Nano-particles, and (3) discovering a high efficiency process for generating silica Nano-particles.
3. The structure, particle size, and textural properties of silica particles derived from crop residues will affect their further application. Silica Nano particles with tunable textural properties have received more attention in wide application in concrete materials, ceramic materials, thermal insulation purposes, adsorption of pollutants in aqueous solutions, biomedical applications, catalysts for synthesizing valuable compounds, chromatography stationary phase, and algae culture growth.
4. The challenges in developing siliceous materials from crop residues are mainly related to silica depletion in soil, segregation approach to energy recovery and silica extraction, and the development of green technologies. Crop residues are promising silica precursors for wide applications through integrated green technological processes that can recover energy, lignocellulosic materials, carbonaceous materials, and of course silica, simultaneously.

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Data Availability The datasets supporting the conclusions of this article are included within the article.

Compliance with Ethical Standards

Conflict of interest The authors declare that they have no competing interests.

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