# Crop residues as potential sustainable precursors for developing silica materials: A review

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# Crop residues as potential sustainable precursors for developing silica materials: A review

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## Abstract

Prospecting sustainable resources will be considerable to generate silica materials which are extensively used for various commercial applications. Accumulated amorphous silica called as phytolith is found in crop residues which are removed during harvesting process. Hence, it will be beneficial to understand the potent of various kinds of crop residues as silica source regarding their global generation, yield of generation, and enhancement by silicon fertilizer. Of the many crop residues discussed in this study, sugarcane leaves are the most prospecting silica source having high value of considered parameters. Various synthesis methods are continuously developed with an expectation to achieve tunable properties of silica particles with high processing efficiency. The applications of silica particles derived from crop residues are varied depending on their unique characteristics related to textural and morphological properties. In addition, the developments of silica materials from crop residues deal with several challenges on silica depletion of croplands, segregation approach of valuable components from crop residues, and high utilization of high energy and chemical reagents. Utilizing industrial wastes containing silica can be promoted as Si fertilizer to heal up silica depletion in croplands. Integrated approach by applying low energy and less chemical methods can be conducted to recover energy, lignocellulosic materials, carbonaceous materials, and siliceous material from crop residues, simultaneously.

**Keyword**: Silica, Crop residues, Sustainable development, Simultaneous recovery

## 1. Introduction

Rapid growth of global population promotes the sustainable production of crop plants to fulfil global food demand [1]. Surely, the generation of residues after harvesting process will be proportional with the productivity of crop plants. High abundant of those crop residues must be handled by applying compatible technological process to recover their valuable components. Many technologies have been employed to utilize organic components of crop residues which can generate renewable energies [2-11], carbonaceous materials [12-21], and lignocellulosic materials [22-31]. However, it will be more advantageous to accomplish those utilization by recovering inorganic matters in ash residues which are mainly consisted of silica.

Silica is well known as a precursor for many applications such as catalysts [32-36], electronic coating [37-41], ceramics [42-46], concrete [47-51], chromatography [52-56], anticorrosion agent [57-60], and optic materials [61-65]. The employment of high purity silica in industrial application will be costly due to the high operating temperature [66, 67]. Thus, the synthesis of silica from crop residues will be a good option to reduce processing cost and counter sustainability challenges. Due to high requirement of silica particle for industrial application including high purity and controllable textural properties, those residues must be subjected into an appropriate technological process for obtaining targeted silica product.

The extraction method of silica are relied on thermal [66, 68-84], physical [85-87], chemical [67, 69, 71, 76, 79, 88-98], or even biological process [84, 99, 100] to obtain silica from crop residues. Typical compositions of inorganic fractions in crop residues require specific technological method to obtain silica particles. Moreover, those methods will determine physical, morphological, and textural properties of the synthesized particles. Therefore, it will be beneficial to classify various methods of silica extraction based on their conception and the advancement toward green and high energy efficiency of processes.

Various silica material can be generated from crop residues such as amorphous silica powder [67, 68, 75, 78, 81, 82, 89, 101-107], silica nanoparticles [79, 92, 93, 96, 108-110], silica xerogel [90, 111], silica aerogel [88, 112-114], mesoporous silica [115-117], and microsphere silica [118-121]. Siliceous materials-based crop residues are widely applied on pollutants removal by absorption and adsorption, drug delivery in biomedical application, cement and ceramic based materials, catalyst for many transformation processes, and filler in composite/membrane fabrication. The expansion of application for these silica materials is certainly required to achieve sustainability in the future. Therefore, a depth analysis can be considered to specify various constraints and opportunities to develop a sustainable silica recovery from crop residues.

This study aims to explore the crop residues which have high potential as silica source, summarize recent technological process for recovering and generating derivative silica product, and specify the silica application from crop residues based on their textural properties. In addition, challenges and future recommendations for developing silica materials from crop residues are discussed.

## 2. The advantageous factors of crop residues as silica precursors

### *2.1. Silica as a major inorganic constituent in crop residue*

Silica has received high attention for agricultural practices due to their beneficial impacts for improving the yields and qualities of a large group of crops. Those beneficial impacts are strongly associated with the silica accumulation behavior which differed 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 [122]. Active transport is tended to allow more transmembrane movement of silica due to the presence of Si transporter proteins such as poly-2-viny pyridine-1-oxide located at the plasma membrane. **Figure 1** illustrate the uptake mechanism of silica and their impact toward agricultural plants. Silica served as insoluble crystalline aluminosilicates in soil which could not be taken up by root plants [122]. Nevertheless, this primary silicate mineral could be weathered and desilicated to liberate dissolved silicon in the form of silicic acid. Silicic acid was taken up from the external solution and released into the apoplast of aerenchyma, and then transported into the stele [123]. It was then translocated to the shoot by transpiration stream through the xylem. Due to large portion of loss water, silicic acid was further concentrated and then polymerized into amorphous phase of silica without any energy at higher than 2 mol L$^{-1}$ of concentration [123]. Proportions and locations of amorphous silica varied with plant species and age of plants. In some cases, amorphous silica could be found in epidermis of leaves, seeds and fruit of trees and herbs and the tissues of leaf blades and inflorescence bracts in grass plants [124]. Mature plants were believed to own largest portion of deposited amorphous silica due to irreversible process of silica deposition in older cell walls.

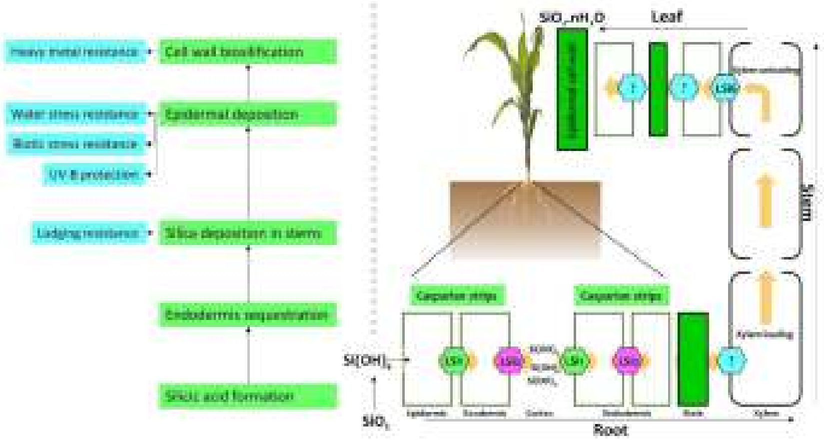

**Figure 1**. Accumulation of silica and their impact on agricultural plants, adapted from Luyckx et al. [125] and Khan et al. [126].

During harvesting process, crop residues in form of husk/hull, straw/stalk, leaf, and bagasse are removed from croplands. To determine the silica content of those residues, the proximate analysis and chemical composition of ash can be considered. In this study, 21 crop residues from 13 agricultural plants have been discussed. As shown in **Figure 2**, crop residues generally possess 60-86 wt.% of volatile matter, 8-31 wt.% of fixed carbon, and 2-24 wt.% of ash [66, 68-70, 74, 76-79, 83, 127-138]. Rice husk, rice straw, and sugarcane leaf are top three in term of ash content, which are reasonably producing more silica particle.

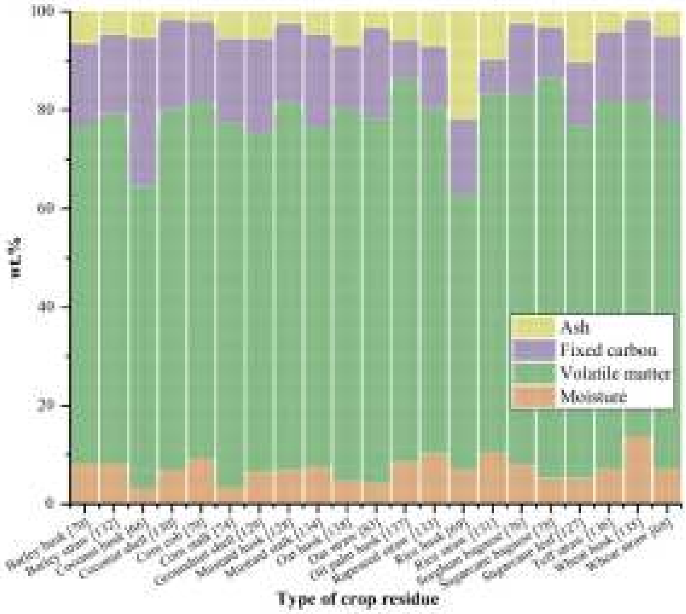

**Figure 2**. Proximate analysis of various crop residues.

Silica exists on 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. [74, 77, 79, 130, 132, 135-151]. As shown in **Figure 3**, crop residues from monocots such as barley, corn, oat, rice, sorghum, and wheat tend to comprise high concentration of silica ranging up to 90 wt.% due to their active silica uptake. Meanwhile, for some dicots classified as intermediate Si-accumulating plants such as groundnut, mustard, and rapeseed, lower silica content up to 50 wt.% can be obtained from their residues with higher concentration of metal alkali impurities. In addition, silica will be more concentrated on pericarp cells rather than stem cells, since the beneficial impact of silica on providing a physical defense by creating more firm/stiff structure on seeds, grain, beans, or kernel. Thus, silica content is even doubled in husks of barley, oat, sorghum, and wheat compared with their straws or stalks.

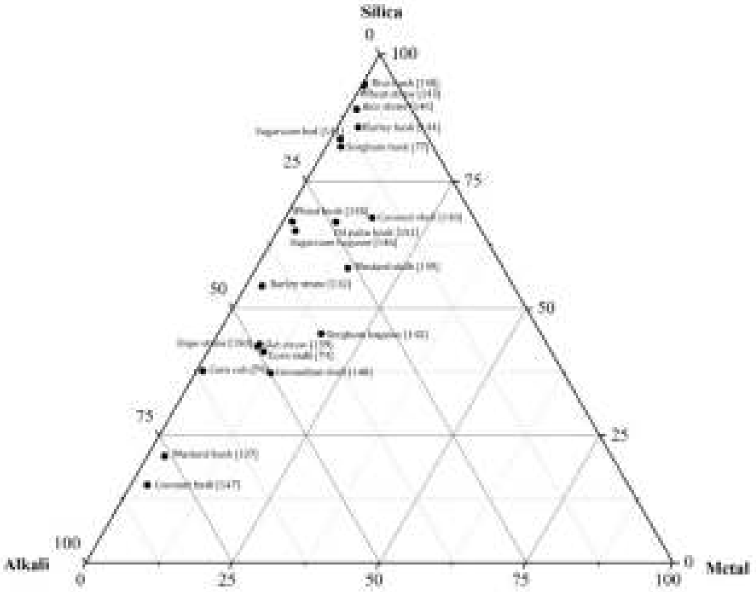

**Figure 3**. Ternary phase diagram of the content of silica, metal, and alkali in various types of crop residues.

### 2.2. *Classified prospect crop residues as silica source*

Determining the prospect silica precursors can be carried out by considering both of yield and productivity of silica which can be derived from crop residues as seen in **Table 1**. The productivity will be associated with extractable silica and harvested area whereas silica yield of each crop residue is determined by considering residue ratio and silica ratio.

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

| Type of crop residue | Residue ratio | Silica ratio | Yield [a] | Crops production [b] | Extractable silica | Harvested area [b], | Productivity |
|---|---|---|---|---|---|---|---|
| | kg residue/ kg crop | g silica/kg residue | g silica/kg crop | million tons/year | million kg/year | million ha | kg/ha year |
| Barley husk | 0.20(1) | 58 | 11.60 | 141 | 1637.94 | 47.01 | 34.84 |
| Barley straw | 0.15(2) | 22 | 3.30 | 141 | 465.96 | 47.01 | 9.91 |
| Coconut husk | 0.35(3) | 5 | 1.75 | 61 | 106.03 | 12.3 | 8.62 |
| Coconut shell | 0.35(4) | 11 | 3.85 | 61 | 233.27 | 12.3 | 18.96 |
| Corn cob | 0.16(5) | 7 | 1.12 | 945 | 1058.70 | 197.19 | 5.37 |
| Corn stalk | 0.50(6) | 19 | 9.50 | 945 | 8980.08 | 197.19 | 45.54 |
| Groundnut shell | 0.30(7) | 19 | 5.70 | 43 | 242.71 | 27.94 | 8.69 |
| Mustard husk | 0.20(8) | 9 | 1.80 | 0.58 | 1.04 | 0.62 | 1.67 |
| Mustard stalk | 0.70(9) | 38 | 26.60 | 0.58 | 15.33 | 0.62 | 24.73 |
| Oat husk | 0.25(10) | 41 | 10.25 | 23 | 239.94 | 10.2 | 23.52 |
| Oat straw | 0.15(11) | 12 | 1.80 | 23 | 42.14 | 10.2 | 4.13 |
| Oil palm husk | 0.35(12) | 37 | 12.95 | 256 | 3313.39 | 21.35 | 155.19 |
| Rapeseed straw | 0.15(13) | 29 | 4.35 | 65 | 283.58 | 34.74 | 8.16 |
| Rice husk | 0.20(14) | 200 | 40.00 | 723 | 28907.17 | 167.24 | 172.85 |
| Rice straw | 1.00(15) | 76 | 76.00 | 723 | 54923.63 | 167.24 | 328.41 |
| Sorghum bagasse | 0.30(16) | 9 | 2.70 | 62 | 166.28 | 40.67 | 4.09 |
| Sorghum husk | 0.15(17) | 31 | 4.65 | 62 | 286.38 | 40.67 | 7.04 |
| Sugarcane bagasse | 0.30(18) | 16 | 4.80 | 1788 | 8583.60 | 25.98 | 330.39 |
| Sugarcane leaf | 0.25(19) | 82 | 20.50 | 1788 | 36659.13 | 25.98 | 1411.05 |
| Wheat husk | 0.20(20) | 92 | 18.40 | 699 | 12866.91 | 218.54 | 58.88 |
| Wheat straw | 0.44(21) | 47 | 20.68 | 699 | 14461.29 | 218.54 | 66.17 |

[a] Computed as a result from residue ratio × silica ratio

[b] Collected from FAOSTAT, http://www.fao.org/faostat/en/#data/QC

(1) Loredo-Cancino et al.[144]; (2) Pallares et al. [132]; (3)Anuar et al. [66]; (4)Islam et al. [152]; (5)Miranda et al. [153]; (6)Zhang et al. [154]; (7)Perea-Moreno et al. [155]; (8)Assumed to be similar with barley husk; (9)Maiti et al. [156]; (10)Thomson et al. [157]; (11,13)Assumed to be similar with barley straw; (12)Assumed to be similar with coconut husk; (14)Azat et al. [69]; (15)Lim et al. [158]; (16)Appiah-Nkansah et al. [159]; (17)Chandraju et al. [160]; (18)Anukam et al. [161]; (19)Kumar et al. [162]; (20)Bledzki et al. [163]; (21)Azocar et al. [164].

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, it can be obtained the value of extractable silica for rice straw and rice husk in the range of 20,000-55,000 million kilograms per year. Although sugarcane leaf has lower silica yield than rice straw and rice husk, high productivity of sugarcane 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 1411 kilogram per hectare, followed by rice straw, sugarcane bagasse, oil palm husk, and rice husk. The other crop residues originated from barley, coconut, corn, oat, rapeseed, sorghum, and wheat have relatively lower silica yield. **Figure 4** presents data plotting of yield and productivity to classify the prospect of various types of crop residues as silica source. Rice straw, rice husk, sugarcane leaf, and oil palm husk are identified as Class 1 of crop residues with high prospect for silica recovery. Class II with intermediate priority of silica recovery encompasses mustard stalk, wheat straw, wheat husk, barley husk, oat husk, corn stalk and coconut husk. Crop residues with low productivity and silica yield are grouped into Class III, including groundnut shell, sorghum husk, rapeseed husk, barley straw, sorghum bagasse, oat straw, mustard husk, coconut husk, and corn cob.

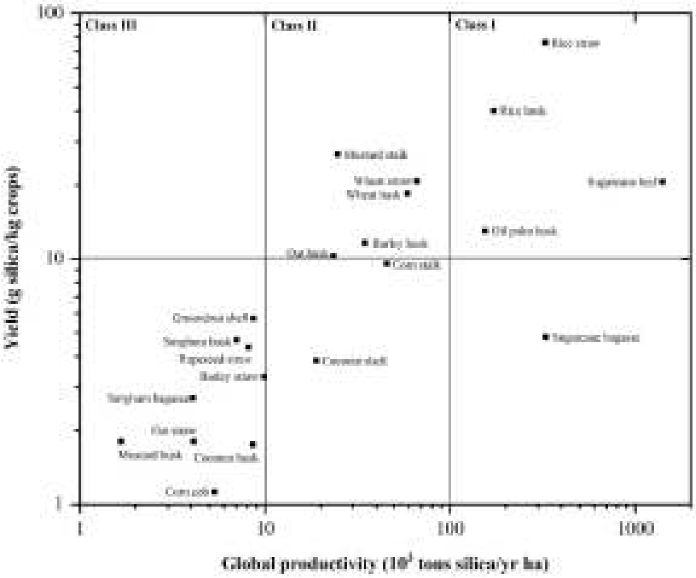

**Figure 4**. Prospecting crop residues based on their silica yield and global silica productivity (data plotting from Table 1).

### *2.3. Effects of silicon fertilizer*

Silicon was known as a beneficial plant nutrient which served a protective system from biotic (pests and diseases) and abiotic stresses. The tolerance against pests and diseases could be available due to the interaction between the host and the pathogen associated with the presence of silicon along with a certain defensive response of plants. Silicon deposition in plants also improved the abrasiveness of the plant tissues which could prevent herbivores and arthropods digesting the plant bodies rich in silicon [165]. Abiotic stress resistance could be defined as an ability being resistance for unexpected conditions mainly due to extreme climate changes. It was provided by mechanical and/or physical protection of deposited silica or biochemical response with different metabolic pathway. The adequate amount of silica could also improve water balance, plant growth and yield, rates of photosynthesis, reproduction and reduce grain chaffness [124].

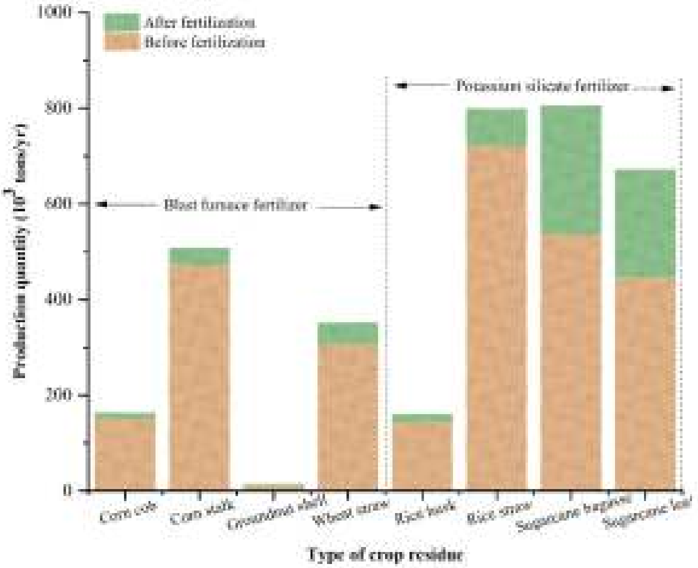

**Figure 5**. Enhancement of crop residues generation by field fertilization of blast furnace slag and potassium silicate [122].

The productivity of crop plants is strived for providing global food security. Because of that, it is insufficient to only rely on the nature of plant growth for producing food commodity. Instead of additional macronutrients for plant growth, silicate fertilizer can also be applied to boost-up the productivity of many agricultural plants. Once the productivity of agricultural plants increases, the generation of residues also rises-up by means enhancing extractable silica enhancement. **Figure 5** tries to illustrate the effect of two Si fertilizer on different crop plants. Enhancement of crop production quantity is ranged from 6 to 14%, 10 to 50% for blast furnace slag and potassium silicate, respectively. These positive response is related to the fact that many crop plants such as rice, wheat, and sugarcane classified as highly Si-responsive plant with large demand of Si [122]. As generation of extractable silica is assumed as much as the crop plants production, it will be considerable to obtain larger amount of silica from crop residues. For instance, Sun et al. [166] reported that application of silicon fertilizer with maximum dosage in the 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.

## 3. Preparation methods for silica particles derived from crop residues

The development of technological process for extracting silica from crop residues can be classified into three levels regarding their conception and advancement as shown in **Figure 6**. The modest concept of silica recovery from crop residues should be obtaining high purity of amorphous particles by combining acid pre-treatment with thermal process. Acid pre-treatment will remove the metal alkali impurities whereas organic fractions will be decomposed by thermal treatment. The next levels of technologies are focusing on tailoring particle size, morphological, and textural properties of silica particles derived from crop residues. Those involve sol gel method, hydrothermal/solvothermal, sonochemical method, and bio-digestion. The latest technologies will be existed to answer the challenges for employing high energy efficiency and environmental-friendly method to produce silica. In this case, laser ablation and microwave sintering are employed as efficient heat source to decompose organic compounds and control textural and morphological properties of silica particles.

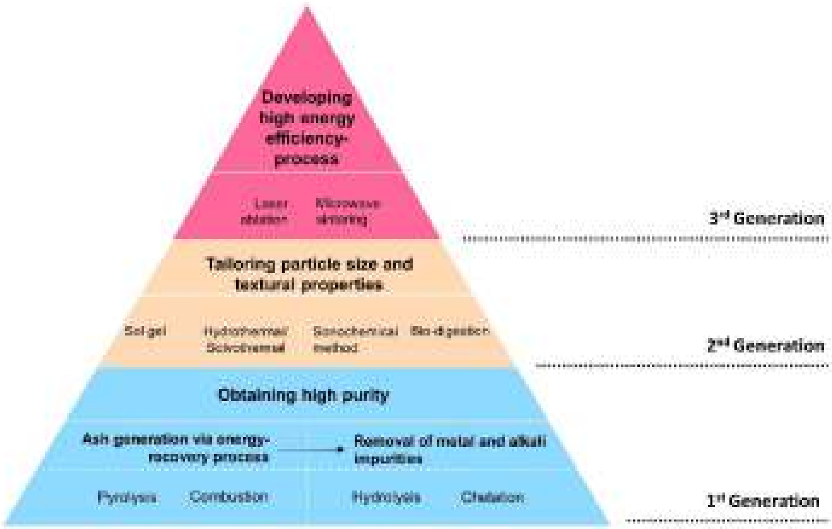

**Figure 6.** Advancement on technological methods of silica extraction from crop residues.

## *3.1. Obtaining high purity of amorphous silica*

### *3.1.1. Removing organic substances of crop residues*

The destruction of combustible portion in crop residues via thermal process 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, operating temperature will be major factor to generate targeted silica particle. Many studies employed thermal process 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 to crystalline. In some case however, high alkali impurities in ash will react with silica then form ternary oxides which promote silica crystallization even at lower temperature. For instance, crystalline phase of silica was obtained by thermal process at 650°C for 3 hours [66]. That was because of the high metal alkali impurities up to 80 wt.% in coconut husk ash which had high possibility to form ternary oxides promoting crystalline structure.

Therefore, thermal method will 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 content of metal alkali impurities.

**Table 2**. Thermal process for silica extraction derived from crop residues

| **Raw material** | **Method** | **Operation condition** | **Silica purity, wt.%** | **Major structure** | **Ref** |
|---|---|---|---|---|---|
| Barley husk | Pyrolysis | 650°C, 8 hours | 85.00 | Amorphous | [70] |
| Coconut husk | Combustion | 650°C, 3 hours | 11.65 | Crystalline | [66] |
| Corn cob | Combustion | 650°C, 2 hours | 34.30 | Amorphous | [79] |
| Corn stalk | Pyrolysis | 620°C | 36.91 | - | [74] |
| Oat straw | Combustion | 1350°C | 31.40 | - | [83] |
| Rice husk | Combustion | 650°C, 3 hours | 97.93 | Amorphous | [80] |
| Rice husk | Combustion | 600°C, 2 hours | 95.77 | Amorphous | [72] |
| Rice husk | Combustion | < 650°C | 91.48 | Amorphous | [81] |
| Rice husk | Combustion | < 780°C | 91.48 | Amorphous | [82] |
| Rice husk | Combustion | 600°C, 2 hours | 72.30 | Amorphous | [75] |
| Rice husk | Combustion | 600°C, 4 hours | 95.60 | Amorphous | [69] |
| Rice straw | Combustion | 500°C, 8 hours | 72.60 | Amorphous | [84] |
| Sorghum bagasse | Combustion | 800°C | 40.16 | Amorphous | [76] |
| Sorghum husk | Combustion | 800°C | 78.19 | - | [77] |
| Sugarcane bagasse | Pyrolysis | 1000°C, 4 hours | 53.10 | - | [78] |
| Sugarcane leaf | Combustion | 650°C | 80.14 | - | [127] |
| Teff straw | Combustion | 900°C, 2 hours | 91.81 | Amorphous | [71] |
| Wheat straw | Combustion | 500°C, 8 hours | 88.09 | Amorphous | [73] |

### *3.1.2. Removing metal alkali impurities*

Since the existence of numerous metal alkali impurities in ash of crop residues during extraction process, many studies tried to modify thermal process by employing acid or alkali pre-treatment to enhance the obtained silica concentration. Hydrolysis and chelation are two common mechanisms which can be employed in this acid treatment. Hydrolysis is frequently applied by utilizing concentrated acid [66, 69, 70, 72, 73, 78, 110, 120, 167] or alkali [66] to remove metal and alkali impurities in ash. On other hand, chelation can eliminate metal alkali impurities by relying on the ability of carboxylic groups in milder acid [69, 104, 168] to chelate metal and alkali ion dissolved in solution.

### Hydrolysis reaction

$2K_{(s)} + 2HCl_{(aq)} \rightarrow 2KCl_{(aq)} + H_{2(g)}$
$2Na_{(s)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + H_{2(g)}$
$2Ca_{(s)} + 2HCl_{(aq)} \rightarrow 2CaCl_{(aq)} + H_{2(g)}$
$2Mg_{(s)} + 2HCl_{(aq)} \rightarrow 2MgCl_{(aq)} + H_{2(g)}$
$2Zn_{(s)} + 2HCl_{(aq)} \rightarrow 2ZnCl_{(aq)} + H_{2(g)}$
$Fe_{(s)} + 2HCl_{(aq)} \rightarrow FeCl_{2(aq)} + H_{2(g)}$

$2K_{(s)} + H_2SO_{4(aq)} \rightarrow K_2SO_{4(aq)} + H_{2(g)}$
$2Na_{(s)} + H_2SO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + H_{2(g)}$
$2Ca_{(s)} + H_2SO_{4(aq)} \rightarrow Ca_2SO_{4(aq)} + H_{2(g)}$
$2Mg_{(s)} + H_2SO_{4(aq)} \rightarrow Mg_2SO_{4(aq)} + H_{2(g)}$
$2Zn_{(s)} + H_2SO_{4(aq)} \rightarrow Zn_2SO_{4(aq)} + H_{2(g)}$
$Fe_{(s)} + H_2SO_{4(aq)} \rightarrow FeSO_{4(aq)} + H_{2(g)}$

### Chelation reaction

$2K_{(s)} + 2C_6H_8O_{7(aq)} \rightarrow 2KC_6H_7O_{7(aq)} + H_{2(g)}$
$2Na_{(s)} + 2C_6H_8O_{7(aq)} \rightarrow 2NaC_6H_7O_{7(aq)} + H_{2(g)}$
$2Ca_{(s)} + 2C_6H_8O_{7(aq)} \rightarrow 2CaC_6H_7O_{7(aq)} + H_{2(g)}$
$2Mg_{(s)} + 2C_6H_8O_{7(aq)} \rightarrow 2MgC_6H_7O_{7(aq)} + H_{2(g)}$
$2Zn_{(s)} + 2C_6H_8O_{7(aq)} \rightarrow 2ZnC_6H_7O_{7(aq)} + H_{2(g)}$
$Fe_{(s)} + 2C_6H_8O_{7(aq)} \rightarrow FeC_6H_6O_{7(aq)} + H_{2(g)}$

**Figure 7** shows the highest silica purity and metal alkali removal efficiency which can be achieved by acid/alkali pre-treatment. The purity of silica particles derived from crop residues are ranged from 88% up to nearly 100% [66, 69, 70, 72, 78, 167, 168] whereas the metal removal efficiencies are in the range of 70-96%. Higher concentration of acid and longer reaction time will be preferable to extract silica from crop residues with relatively low silica content such as barley straw, coconut husk, and wheat straw [66, 70, 73]. It will be beneficial to strongly reduce the higher metal alkali content in those crop residues.

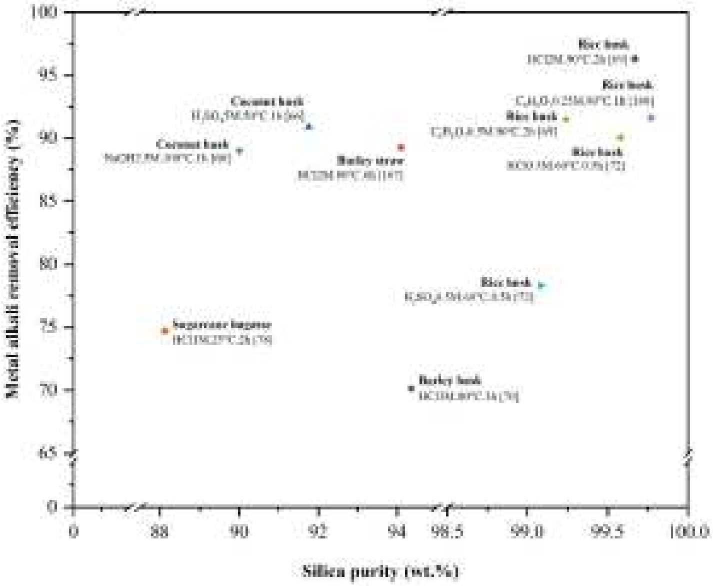

**Figure 7.** Silica purity and removal efficiency of metal alkali impurities obtained by acid pre-treatment.

Chelation reactions by using citric acid also exhibit relatively high removal efficiency for metal and alkali impurities, especially for crop residues with high silica content like rice husk. Umeda and Kondoh [168] obtained 99.77% of purity of silica and removal efficiency of metal alkali impurities up to 92% by chelation process using 5 wt.% of citric acid at 80°C for 3 hours. On other hand, Azat et al. [69] applied facile chelation method by dry mixing of rice husk with 10 wt.% citric acid to obtain 98.67 of silica purity with 91.51% of metal alkali removal efficiency.

### *3.2. Tailoring textural properties of nano-sized silica particle derived from crop residues*

#### *3.2.1. Hydrothermal/solvothermal*

Silica nanoparticles with tunable textural properties can be generated from crop residues by using hydrothermal [108, 109, 120, 169, 170] and solvothermal process [102, 171]. In general, solvothermal must be identical with hydrothermal, except that organic solvents instead of water are employed to carry out reaction. These methods are being able to speed up reaction among the reactants which is hydrolysis between reaction media and metal alkali impurities in crop residues. Moreover, self-assembly of nanomaterials in the solution will also be obtained as further stage in these methods [172]. As seen in **Table 3**, 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 of temperature and 0.01-0.1 MPa of pressure. Meanwhile, solvothermal used absolute ethanol as reaction media to synthesize silica at 180-190°C of temperature and 0.1 MPa of pressure. By increasing temperature and pressure to its critical point, expected substances can be completely dissolved in the solvents [173]. In the final stage, the treated crop residues are dried and calcined at set temperature to release water and solvents and remove organic compounds.

**Table 3**. Hydrothermal process on silica extraction

| Raw material | Process condition | Final product | Ref |
|---|---|---|---|
| Rice husk | $C_6H_8O_7$ 10% 150°C, 0.01 MPa, 3 h | Silica nanoparticles (249-250 nm) | [169] |
| Rice husk | $CH_3COOH$ 10% 150°C, 0.01 MPa, 3 h | Silica nanoparticles (274-295 nm) | [169] |
| Rice husk | 0.2 M $H_3PO_4$ 150°C, 0.01 MPa, 3 h | Silica nanoparticles (239-242 nm) | [169] |
| Rice husk | 1 M HCl 120°C, 0.1 MPa, 2 h | Silica nanoparticles (10-30 nm) | [108, 109] |
| Rice husk | Ethanol 180°C, 0.1 MPa, 24 h | Amorphous silica (101 $m^2/g$ of specific surface area) | [102] |
| Rice husk | Ethanol 190°C, 0.1 MPa 16 h | Porous silica | [171] |
| Sorghum husk | 120°C, 0.1 MPa, 2 h | Amorphous silica (spherical, saddle, and dumbbell shape) | [120] |

### *3.2.2. Sol gel method*

Sol gel method has been widely applied to generate silica particle from crop residues as seen in **Table 4**. It can be carried out through hydrolysis and polycondensation to obtain sol/gel form of silica [174]. Fresh crop residues are often pre-treated by using thermal [67, 71, 79, 88, 89, 95, 96], acid/alkali treatment [91, 175], or combination of acid treatment and calcination [69, 76, 90, 92-94, 97, 98, 107, 176, 177] to eliminate unexpected impurities before subjected into sol gel method. Once the pre-treated crop residue is obtained, sol gel process may begin as following reactions:

$$NaOH + SiO_2 \rightarrow Na_2SiO_3$$

$$KOH + SiO_2 \rightarrow K_2SiO_3 \tag{1}$$

$$3Na_2SiO_3 + 2H_3PO_4 \rightarrow 3SiO_2 + 2Na_3PO_4 + 3H_2O$$

$$Na_2SiO_3 + H_2SO_4 \rightarrow SiO_2 + Na_2SO_4 + H_2O$$

$$Na_2SiO_3 + 2HCl \rightarrow SiO_2 + 2NaCl + H_2O \tag{2}$$

Firstly, silica powder is subjected into alkali oxide solution like NaOH [67, 69, 71, 76, 79, 88, 90-96, 98, 175-177] or KOH [89, 107] to obtain transparent silicate solution. Then, concentrated acid such as $H_3PO_4$ [175, 177], $H_2SO_4$ [91, 92, 94, 95], or HCl [67, 69, 71, 76, 79, 88-90, 96-98, 107, 176] is added dropwise to begin the hydrolysis process. Those acids cause the formation and condensation of ≡Si–OH which can form dimers dimmers or trimers followed by their growth into particles [175]. Formation of silica particle is frequently assisted by aging process at room temperature for a set time [67, 71, 76, 79, 88, 92, 94, 107, 177]. In the final stage, the sol/gel is dried and ground to obtain silica powder.

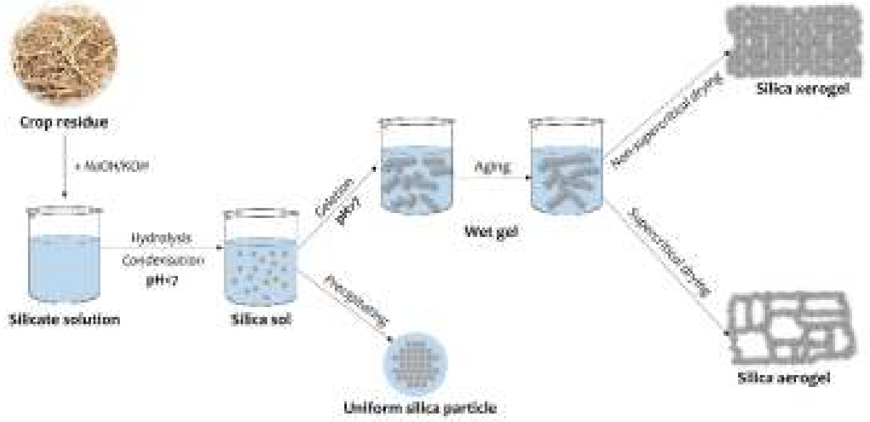

**Figure 8.** Schematic process of silica synthesis via sol gel method derived from crop residues.

As seen in **Table 4**, sol gel method successfully generates amorphous silica nanoparticle, silica xerogel, and silica aerogel from various crop residues. The key factors for those silica properties involve pH value, aging time, aging temperature, and dispersing agent [175, 178]. The pH value will be responsible to promote particle growth and formation of spherical shape. Many studies used pH value at the range of 7-9 to ensure silica particle formation (see **Table 4**). Zulfikar et al. [175] reported that silica suspension becomes very dilute at pH lower than 7 while agglomeration of silica particle will be carried out at pH larger than 9. Instead of pH adjustment, aging time and temperature must be concerned to achieve high stability of colloids which can promote the formation of nanosized and uniform size distribution of particles. Le et al. [178] have proved the effect of aging temperature and time on the stability of silica nanoparticles with the presence of dispersing agent. As temperature increases from 30°C to 60°, the interaction between hydroxyl group on silica surface with dispersing agent will be increase which leads to generate better uniform distribution. At temperature higher than 80°C however, adsorbed dispersing agent molecules at hydroxyl group of silica will be desorbed, exposing reverse effect on particle size distribution. The increase of aging time may affect to narrow particle size distribution, but it must be noted that the set time must be able to achieve dissolution equilibrium ensuring better dispersion of silica particle in the solvents.

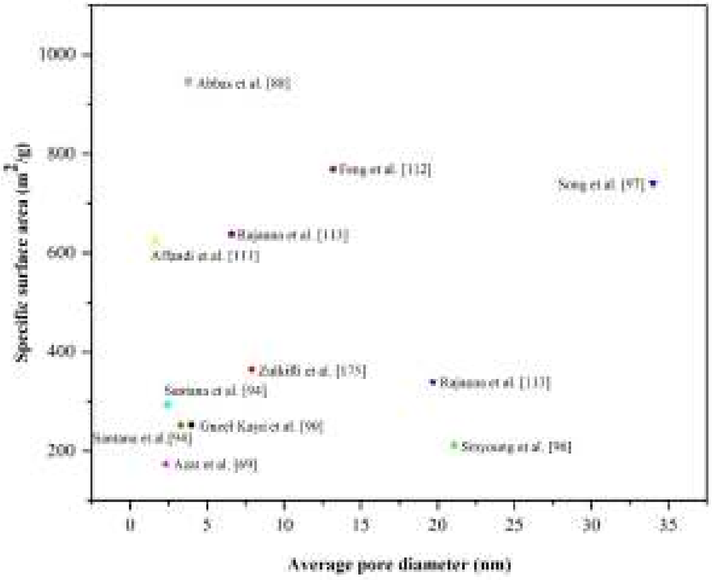

**Figure 9**. Textural properties of silica xerogel and aerogel derived from crop residues

Xerogel and aerogel are two state of silica resulting in sol gel method which can be affected by drying process. Xerogels refer to a solid formed by evaporative drying of gel with an unhindered shrinkage [172]. Once supercritical drying is applied to remove solvents, that solid called as aerogel. In case of silica-based crop residues, a few studies clearly stated their targeted particle as silica xerogel or aerogel. Guzel Kaya et al. [90] studied the synthesis of silica xerogel from corn stalk ash in ambient pressure drying by sol gel method. That silica xerogel retain 0.048 g cm$^{-3}$ of bulk density, 252 m$^2$ g$^{-1}$ of surface area, 0.900 cm$^3$ g$^{-1}$ of pore volume, 4 nm of pore diameter, and 0.040 W m$^{-1}$ K$^{-1}$ of thermal conductivity. Previously, Affandi and co-workers [111] had successfully synthesized high-purity silica xerogels from sugarcane bagasse ash. The specific surface area, pore volume, and pore diameter of that silica xerogel ranged from 69 to 152 $m^2$ $g^{-1}$, 0.059 to 0.137 $cm^3$ $g^{-1}$, and 3.2–3.4 nm, respectively. Silica aerogel generally possess higher surface area, larger pore volume and pore diameter. Rajanna et al. [113] reported that granular silica aerogel from rice husks poses 637.6 $m^2$ $g^{-1}$ of specific surface area, 1.2 $cm^3$ $g^{-1}$ of pore volume, and 6.6 nm of pore diameter. Abbas et al. [88] also investigated the properties of silica aerogel derived from rice husk which are slightly different. That silica aerogel exhibits 769 $m^2$ $g^{-1}$ of specific surface area, 2.81 $cm^3$ $g^{-1}$ of pore volume, and 13.2 nm of pore diameter. Other silica xerogels derived from rice husk had been successfully obtained by Feng et al. [112], showing 945.8 $m^2$ $g^{-1}$ of specific surface area, 0.899 $cm^3$ $g^{-1}$ of pore volume, and 3.80 nm of pore diameter.

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

| Raw material | Preliminary method | Silicate formation | Sol gel | | | Final product | Ref. |
|---|---|---|---|---|---|---|---|
| | | | 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 | [67] |
| Corn cob | Calcination | 1 N NaOH boiled 3 h | 1 N $H_2SO_4$ to pH 7 and 10 | - | Air drying at 80°C for 24 h | Silica nanoparticle | [95] |
| 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 | [79] |
| Rice husk | Acid leaching, calcination | 2 M NaOH 90°C 2 h | 85% $H_3PO_4$ to pH 7 in the presence of ethanol | 30 min 25°C and 65°C | Hot water washing, calcination | Silica nanoparticle | [177] |
| 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 nanoparticle | [69] |
| Rice husk | Acid leaching, calcination | 0.1 M NaOH | $NH_4OH$ to turbid color | - | Air drying at 80°C for 24 h | Silica nanoparticle | [93] |
| Rice straw | Acid leaching | NaOH (2.0%, w/v) 100°C 3 h | 1.5% (v/v) $H_2SO_4$ to pH 6.5 | - | Air drying | Silica nanoparticle | [91] |
| Corn stalk | Acid leaching, calcination | 3M 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 | [90] |
| Rice husk | Acid leaching | 10 wt.% NaOH 90°C 1 h | 3 M $H_3PO_4$ to pH 7-9 | - | Freeze drying, calcination | Silica xerogel | [175] |
| 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 | [96] |
| Rice husk | Acid leaching, calcination | 1.5 M NaOH 90°C 1 h | 1 M HCl to pH 7 | 70°C 1-7 days | Air drying at 70°C for 48 h | Silica xerogel | [97] |
| Rice husk | Acid leaching, calcination | 4 M NaOH 80°C 4 h | 5 M $H_2SO_4$ to pH 9 | 30 min at 25°C | Air drying at 80°C for 24 h | Silica xerogel | [94] |
| 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 | [69] |
| 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 | [111] |
| 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 | [71] |
| Rice husk | Calcination | 1 N NaOH 90°C 2 h | 1 N HCl to pH 2-3; kerosene + dual surfactant; $NH_4OH$ to pH 7 | 1 h at 25°C | Supercritical $CO_2$ drying at 150 bar 50°C for 8 h | Silica aerogel | [113] |
| Rice husk | Calcination | 1 M NaOH 100°C 3.5 h | 1 M $NH_3$ to pH 4-6 | - | Ambient pressure drying at60°C for 2 h | Silica aerogel | [112] |
| 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 | [88] |

### *3.2.3. Sonochemical method*

Further processing methods are being required during silica synthesis to obtain microstructural size and surface-to-volume ratio of the silica nanoparticles. Sonochemical method presents as an emerged technique to generate those required properties. It utilizes high intensity ultrasound to create acoustic cavitation which can generate high temperature and high pressure at the center of exposed area [172]. Those conditions will produce hydrogen and hydroxyl radicals in aqueous solution which are then diffused into liquid, increasing nucleation and growth rate with better size distribution. In sol gel process, those radicals are produced in hydrolysis stage which enhance condensation and decrease overall reaction time.

In case of silica synthesis from crop residues, sonochemical method used to assist acid leaching and combustion process [86] and sol-gel method [87], producing size-controllable nanoparticles. Salavati-Niasari and Javidi [87] utilized high-intensity ultrasound (600 W at 20 kHz) to synthesize silica nanoparticle from rice husk. Their study implies that controllable particle size of silica can be achieved at 10-30 min of sonication. Longer sonication time will promote aggregation of nanoparticle caused by shock wave with high pressure, micro-emission fluid and "Brown phenomenon" of nanoparticle itself. Sankar et al. [86] investigated further effect of sonication time on textural properties of silica nanoparticle 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 to enhance porosity of silica nanoparticle. Specifically, the synthesized silica nanoparticles possess 271.22 $m^2\ g^{-1}$ of specific surface area, 0.306 $cm^3\ g^{-1}$ of pore volume, and 4.11 nm of average pore size.

### *3.2.4. Bio-digestion method*

The employment of bio-digestion process for extracting silica from crop residues is identical with sonochemical method in term of controlling nanosized particle of silica. Bio-digestion relies on the ability of organism [99, 100] or even microorganism [84] to degrade the organic matter via enzymatic hydrolysis and generate silica nanoparticle through mechanical works produced by their digestion organs. Further processes such as calcination and acid leaching are required after bio-digestion to remove organic matters and metal alkali impurities of resulted humus, respectively. Torres et al. [100] argued that vermicomposting techniques are preferable to achieve specified crystal arrangement of silica particle. It is related to the different size and shape of phytolith as the result of diverse chemical structure that present in plants such as proteins, lignin and polysaccharides. Red wiggler worms are preferable in vermicomposting to obtain silica particle from crop residue due to their unique characteristics: eat their weight daily, excrete 60% of the ingest as humus, show prolific profile, poses longer life time up to 16 years, resist aggressive environments, and can digest crop residues that contain high concentration of silica [99, 100]. Esteves et al. [99] use a wood container (45 × 30 × 22 cm) with 5000 red worms to produce humus from rice husk by digestion process for 1 month. That process can achieve 88% production efficiency with 55-250 nm of particle size of silica. Other study conducted by Torres et al. [100] employ a small-scale system made of hemlock wood (50 × 35 × 25 cm) with 1000 red worms to generate silica nanoparticle from nixtamalized corn for two month processing. This experimental setup can achieve 90.21% of production efficiency which means higher than previous study. Moreover, the resulted silica particle exhibits hemispherical shape with size of 100 nm. Further analysis reported that it can defined as mesoporous silica with 9.1 $cm^2$ $g^{-1}$ of specific surface area, 0.027 cm$^3$ g$^{-1}$ of pore volume, 18.4 % of porosity, and 11.99 of average pore diameter.

### 3.3. *Pursued method for achieving high energy efficiency and low environmental impact*

#### 3.3.1. *Laser ablation*

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

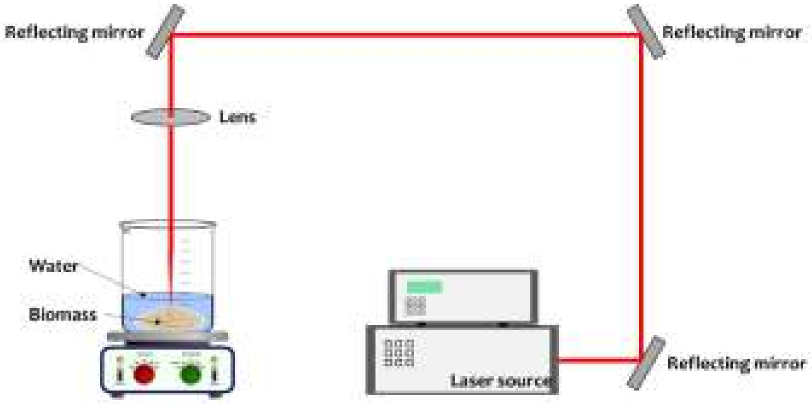

**Figure 10.** Schematic process of laser ablation for silica extraction from crop residues, adapted from Rawat et al. [179].

San et al. [85] utilize this method to synthesize silica nanoparticle from sugar beet bagasse. The generation of silica nanoparticle have achieved by employing 16 mJ of pulse energy to remove organic compounds in sugar beet bagasse. That energy has achieved by conducting a commercial nanosecond 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 a size range of 38–190 nm with an average size of ~74 nm.

### *3.3.2. Microwave sintering*

Microwave sintering is well known as the most popular energy source to heat dielectric materials in industrial application with high efficiency on processing time and energy consumption [180]. Microwave is basically electromagnetic energy with frequency in the range of 300 MHz to 300 GHz [172]. In case of silica synthesis from crop residues, that heat energy will be useful for transforming amorphous silica into its crystalline phase [180] or assisting sol gel method to promote nucleation and nanoparticle growth [181].

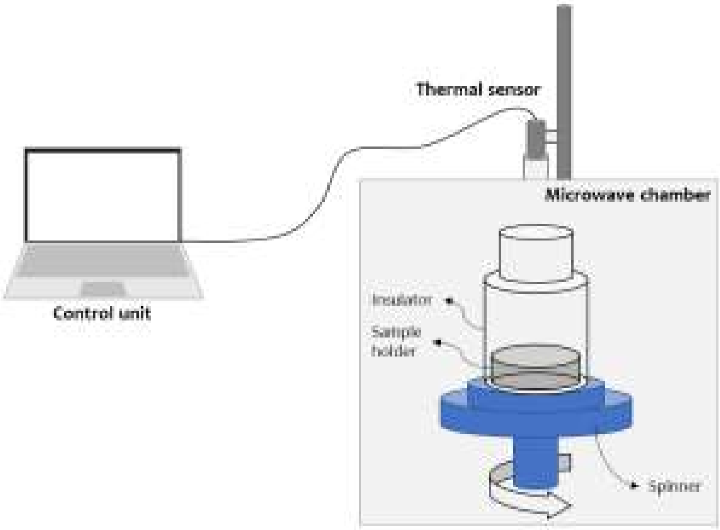

**Figure 11.** Microwave sintering for silica extraction from crop residues, adapted from Makul et al. [180].

Makul et al. [180] investigated the properties of silica particle prepared from rice husk ash using rapid 2.45 GHz microwave sintering at temperature range 800-1200°C. The resulted silica particles are observed as $SiO_2$-cristobalite and some of $\alpha$-$SiO_2$. Increasing temperature up to 1100°C will completely remove amorphous phase of silica. Other study by Pijarn et al. [181] used microwave radiation at 300 W for 60 min to assist sol gel method producing silica gel from rice husk. Silica gel produced by this method exhibits 50-70 nm of particle size, 10-30 nm of pore size diameter, 0.7-1.0 $cm^3 g^{-1}$ of pore volume, and 400-700 $m^2 g^{-1}$. These textural properties are not significantly different with commercial silica gel tested in that study.

## 4. Recent progress on application of silica material derived from crop residues

The typical properties of silica particle will determine its compatibility on certain application field. Figure 5 shows the correlation between synthesis method, achieved properties, and the application of silica particle derived from crop residues.

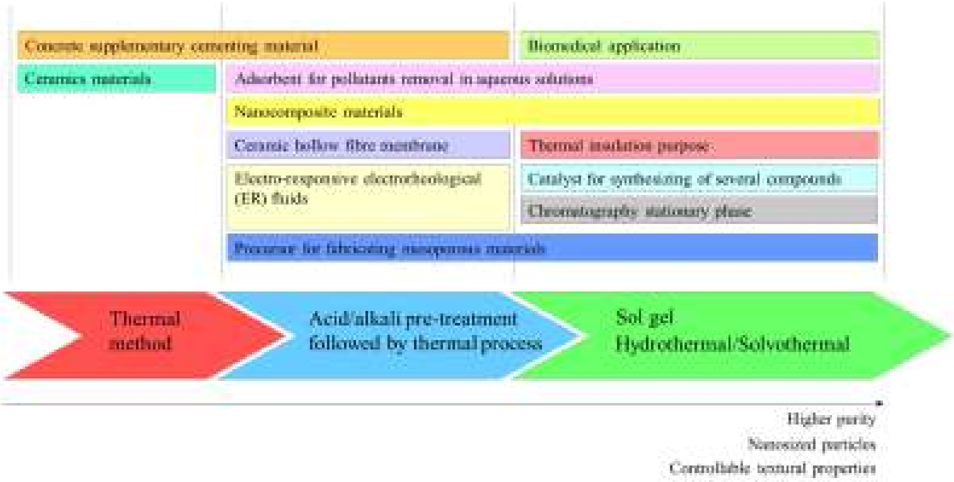

**Figure 12**. Various applications of silica derived from crop residues based on their preparation methods and characteristics

Amorphous silica particles prepared by thermal method is frequently applied on fabrication of concrete and ceramics. By enhancing their purity, it will be possible to apply them on preparation valuable materials such as high-quality concrete, adsorbent, composite, membrane, ER fluids, and mesoporous material precursor. Additionally, pure silica nanoparticle will be required on biomedical application, thermal insulation purposes, catalyst fabrication, and chromatography stationary phases.

### *4.1. Concrete materials*

Many studies investigated the improvement on mechanical performances of concrete by the presence of amorphous silica particle derived crop residues as partial replacement for ordinary concrete materials. Carreno et al. [80] reported that compressive strength values of 755.06 kg f $cm^{-2}$ can be obtained at 28 days by replacing 40% of cement with micro-milled RHA material treated at 650°C. Other study conducted by Amin et al. [68] also reported that significant improvement of strength, stiffness, toughness, and ductility can be observed in concrete containing 15 wt.% wheat straw ash at 91 days. The ash of crop residue can also be mixed with other materials to partially replace cement in concrete fabrication. Pandey and Kumar [145] mixed rice straw silica along with commercial micro-silica as partial replacement for Ordinary Portland Cement (OPC) to improve mechanical strength of Pavement Quality Concrete (PQC). Maximum compressive, flexural and tensile strength are found when OPC was partially replaced by 5%–7.5% of rice straw silica and micro-silica composite. Sorghum husk ash also mixed with Laterite to partially replace Ordinary Portland Cement (OPC) up to 20% in concrete construction [182]. Unfortunately, the compressive strength is insufficiently improved at early curing time.

The distinct role taken by silica particle derived from crop residues in concrete development. Sinyoung et al. [96] utilized silica nanoparticles derived from ash of rice husk to synthesize belite cement by firing with two different calcium sources (calcium carbonate and calcium nitrate). That silica nanoparticle is sufficiently reactive to form the principal phase in belite cement (larnite or b-$C_2S$) at temperatures 800°C, especially with calcium nitrate as the calcium source. On other hand, Junaidi et al. [104] was successfully synthesized superhydrophobic 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 is considerable for further improvement to enhance its practical use in construction and building application.

### *4.2. Refractory ceramic materials*

Silica particle derived from crop residues is certainly observed as amorphous structure. The crystallization process at temperature higher than its melting point can generate crystal phase of silica like quartz, cristobalite, tridymite, etc. Fernandes et al. [183] reported that thermal treatment at 1000°C will be affordable to obtain mainly silica with the crystalline phases cristobalite and tridymite. These silica crystals will be beneficial components for preparing refractory ceramics. Furthermore, that silica particle can also be incorporated with other ceramic reinforcement materials in the different form of aluminum matrix to achieve good combination of strength and ductility [105].

Several studies have been carried out to investigate the possibility of silica derived from crop residue fabricating refractory ceramics by replacing kaolin clay. Sobrosa et al. [81] developed refractory ceramic materials by replacing kaolin clay with rice husk silica at different volume percentages. The use of 10% silica resulted in increase the mechanical strength without decreasing the thermal shock strength. The effect of rice husk silica on the mechanical and thermal properties of refractory ceramic materials is also investigated by Stochero et al. [82]. 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 on the mechanical and thermal properties of refractory ceramics can be obtained by replacing kaolin clay with rice husk silica and steel fibers. Other studies have been conducted to fabricate glass-ceramic tiles by using rice husk as silica precursors. Glass-ceramic tiles are successfully developed by Andreola et al. [184] by a sinter-crystallization process at 900°C using a glassy frit formulated in the MgO-$Al_2O_3$-$SiO_2$ composition system. Those ceramic materials exhibit higher bending strength and Mohs hardness compared with commercial glass-ceramics.

### *4.3. Thermal insulation purposes*

The extracted silica particles from crop residue can be derived into refractory materials which have enhanced thermal and acoustic insulation performance. Amorphous rice husk silica has been investigated to prepare forsterite refractory and refractory cordierite which are have beneficial characteristics as thermal insulator. Hossain et al. [185] investigated the effect of amorphous rice husk silica on the phase formation and the physical characteristics of forsterite refractory prepared from quartz and MgO powder at 1100°C of sintering temperature. Better reaction between amorphous silica and periclase which promotes formation of forsterite phase will be increased at higher loading of rice husk silica. The presence of forsterite phase results in the decrease density, porosity, and thermal conductivity which are affordable for thermal insulation purposes. Other study by Sembiring et al. [107] prepared refractory cordierite from rice husk silica, $Al_2O_3$, and MgO powders at sintering temperature range of 1050-1035°C. At that temperature range, the spinel and cristobalite of raw materials will transform into cordierite followed by decrease in density, porosity, and thermal expansion coefficient.

In addition, a new thermal and acoustic insulation material is successfully prepared from corn stalk silica [90]. Silica xerogel is firstly synthesized from corn stalk ash in ambient pressure drying by sol gel method. This silica xerogel is then used to fabricate silica xerogel/epoxy nanocomposites. Higher amount of silica xerogel in the neat epoxy resin not only enhances thermal stability, but also reduces thermal conductivity of the epoxy nanocomposites. The presence of 1.5 wt.% silica xerogel will decrease acoustic velocity from 2541 m/s to 2373 m/s. A slight increase on water sorption of the epoxy nanocomposites will be obtained with addition of silica xerogel. Those mentioned characteristics of the epoxy nanocomposites will be suitable for thermal and acoustic insulation purposes.

### *4.4. Adsorbent for pollutant removal in aqueous solutions*

Gadolinium (Gd (III)), mercury (Hg (II)), lead (Pb (II)), and ciprofloxacin drug are kind of pollutants in aqueous solutions which can be handle by silica materials derived from crop residues. Silica powder and silica gel derived from rice husk ash are successfully utilized to prepare polymer and grafted copolymers for adsorption of gadolinium [89]. The result indicates that silica gel grafted copolymer possess maximum Gd (III) adsorption capacity of 229.36 mg/g which is higher than the other adsorbent used in adsorption of Gd (III) in other works. Hg(II) adsorption process can be carried out by using NaA zeolite derived from barley husk ash [70]. That zeolite material will be promising adsorbent $Hg^{2+}$ ions removal from the aqueous solutions indicated by high adsorption efficiency as great as 98%. Other study by Hassan et al. [186] 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 the aqueous solution. It is indicated by good adsorption-desorption for five cycles with reduction in percentage of Pb (II) removal from 75% to 43%, and 65% to 27%. In addition, the nanostructure of silica derived from rice husk has a good adsorption capacity for the removal of ciprofloxacin drug from aqueous media [92]. That silica nanoparticle shows a maximum ciprofloxacin adsorption capacity at 190 mg/g which is much higher than that of commercial silica gel (11.0 mg/g), under the same optimum conditions.

### *4.5. Biomedical application*

Application of silica particles derived from crop residues on biomedical is strongly dependent to their compatibility with human mesenchymal stem cells [108, 109, 120]. Biocompatibility assessment have been conducted by Alshatwi et al. [108] and Athinarayanan et al. [109] to determine the potential of biogenic silica nanoparticle derived from rice husk on biomedical application. Those studies reported that biogenic silica nanoparticles prepared from rice husk are applicable on bone tissue engineering due to their excellent compatibility toward human mesenchymal stem cells. Periasamy et al. [120] tried to investigate the biocompatibility of silica nanoparticle derived from other crop residue that is sorghum husk. The harvested silica particle from sorghum husk is observed as amorphous solid with spherical, dumbbell, saddle, and sinuous shapes 10 – 200 µm. It is also claimed as nontoxic material with excellent biocompatibility with human mesenchymal stem cells which has high potential not only for tissue engineering in biomedical fields.

Other biomedical applications of silica derived from crop residues are studied by Rajanna et al. [113] and Prabha et al. [93]. Hollow silica aerogel microspheres derived from rice husk are considerable as good drug delivery vehicles, indicated by a fast release of ibuprofen from loaded that silica particle compared to pure crystalline ibuprofen and other loaded forms [113]. On other hand, an UV-Vis spectroscopy analysis indicated that silica nanoparticle derived from rice husk is considerable for bioimaging application indicated by the photoluminescence emission at visible region. Hence, it is possible to utilize that material for theranostic applications by good arrangement of drug conjugation on the surface of nanoparticle [93].

### *4.6. Catalyst applications*

The application of crop residues-derived silica particle on catalyst synthesis for generating valuable compounds have been widely investigated. Salakhum et al. [79] prepared hierarchical faujasite nanosheets using corn cob ash-derived nanosilica in the presence of a hierarchical porogen. The obtained materials show outstanding catalytic properties for the hydrogenation of lignin-derived alkylphenols. Other study by Davarpanah et al. [101] has been conducted to synthesize nano acid catalyst derived from rice husk silica for the synthesis of 3,4-Dihydropyrimidinones/thiones compounds. This nano catalyst shows several advantages which are related to excellent yields of targeted product in a short period of time and its flexibility in recovery process. In addition, rice husk silica can also be applied on the preparation of homemade biocatalyst via physical adsorption of lipase for optimizing enzymatic synthesis of a cosmetic ester [171]. That homemade biocatalyst exposes high catalytic activity in solvent and solvent-free systems and operational stability which are potential for further application in industrial scale of cosmetic ester synthesis.

Rice husk silica can also be employed as supporting materials for iron catalysts to conduct heterogenous fenton degradation for oxalic acid [103] and organic dyes [98]. Great catalytic activity of those materials will be related to the nature of mesoporous structure of silica which can provide sufficiently cavities and surface area, creating more active sites for targeted compounds. Distinct mechanism of dye degradation has been carried out by using carbon-containing $SiO_2$-based photocatalysts prepared from husks-derived biogenic silica by solvothermal method. Rice husk silica-derived catalyst exhibit higher adsorption capacity, indicating that RhB adsorption is carried out through basic mechanism via interactions between hydroxyl groups in the surface of $SiO_2$ with the cationic species on dye compounds [102]. Similar adsorption mechanism is also obtained by Velmurugan et al. [67] when amorphous silica from corn cobs utilize to adsorb methylene blue. In that process, extracted silica acts as an electron transfer mediator between silica particles and methylene blue by acting as a redox catalyst.

### *4.7. Other valuable applications*

Shahnani et al. [121] utilized silica derived from rice husk for stationary phase of chromatography. Microsphere silica is prepared by sol gel method with the presence of nonionic surfactant, P123. The prepared silica microsphere is then packed with an analytical column to evaluate the separation of 10-deacetylbaccatin III and rutin from taxol and hesperidin, respectively. 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 nanoparticle have also been applied in fabrication of electro-responsive electrorheological (ER) fluids. Kwon et al. [110] investigated ER properties of the 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 nanoparticles can be considered as a promising component of ER fluid.

## 5. Challenges on developing silica materials from crop residues

### *5.1. Silica depletion in soil due to crop residues utilization*

Phytolith is a typical term to specify deposited amorphous silica in intracellular or extracellular compartments of plant. It is known as major component of biogenic silica along with zoogenic, protistic, and microbial silica components in soil [187]. As shown in **Figure 13**, phytolith is involved in 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 concentration of phytolith will be removed from crop lands during harvesting process. The removal of phytolith from crop lands will interfere biogeochemical silicon cycle in croplands by interrupting the replenishment of silicic acid in soil. This condition provokes routine application of silicate fertilizer to heal up the availability of silica in soil. It may increase the production cost but sometimes retain the soil pollution by chemical fertilizer.

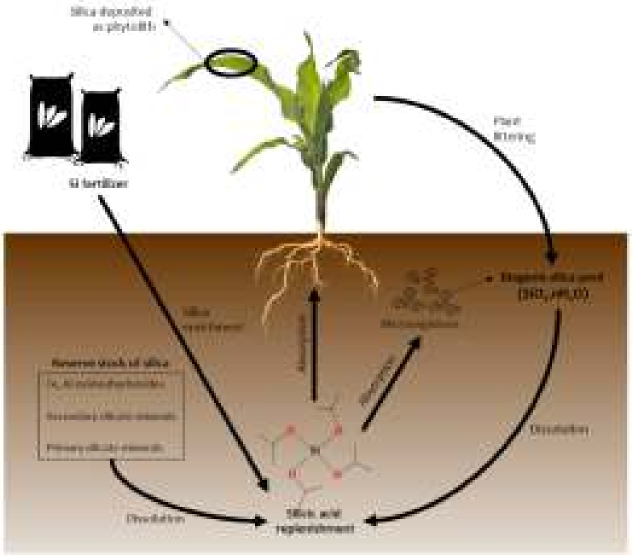

**Figure 13**. Biogeochemical silica cycle in croplands.

Silica depletion on croplands becomes a critical issue for synthesizing silica from crop residues into various siliceous products. Development of Si fertilizer from other sustainable sources become a decent option to overcome this dilemmatic condition. Many studies have been investigated to utilize various industrial wastes as Si fertilizer for crop plants. Haynes et al. [188] evaluated four kinds of industrial wastes (blast furnace slag, steel slag, processing mud, fly ash) as sources of fertilizer silicon for paddy rice plant. 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 highly silica content such as sewage sludge [189], waste silicon sludge [190], silicon kerf waste [191], waste products of the phosphate fertilizer industry [192] may also be considered as fertilizer-Si sources.

### *5.2. Segregated approach on recovery of valuable components in crop residues*

Various silica materials with compatible properties have been synthesized from crop residues by considerable methods. Those methods are mostly applied segregated approach to recover valuable compounds of crop residues. During silica extraction, organic compounds and metal alkali impurities as unexpected matters are removed thrown away without further processing. Therefore, it will be preferable to conduct an integrated technological method to completely recover valuable components in crop residues. Several studies have been carried out to synthesize silica along with conversion process toward organic compounds of crop residues. Zhang et al. [193] consecutively preparation of d-xylose and pure superfine silica from rice husk. Similarly, Barana et al. [28] and Krishania et al. [26] have employed same idea to prepare silica along with lignocellulosic material from rice husk and rice straw, respectively. Further investigation by Zhang et al. [194] improves their previous study to obtain d-xylose, organosolv lignin, ethanol and amorphous superfine silica, simultaneously. Other studied by An et al. [195] and Liu et al. [196] can synthesize activated carbon from rice husk ash along with silica extraction. In addition, autothermal fluidized bed gasification of rice husk have been conducted by Thakkar et al. [176] to extract silica and energy, consecutively.

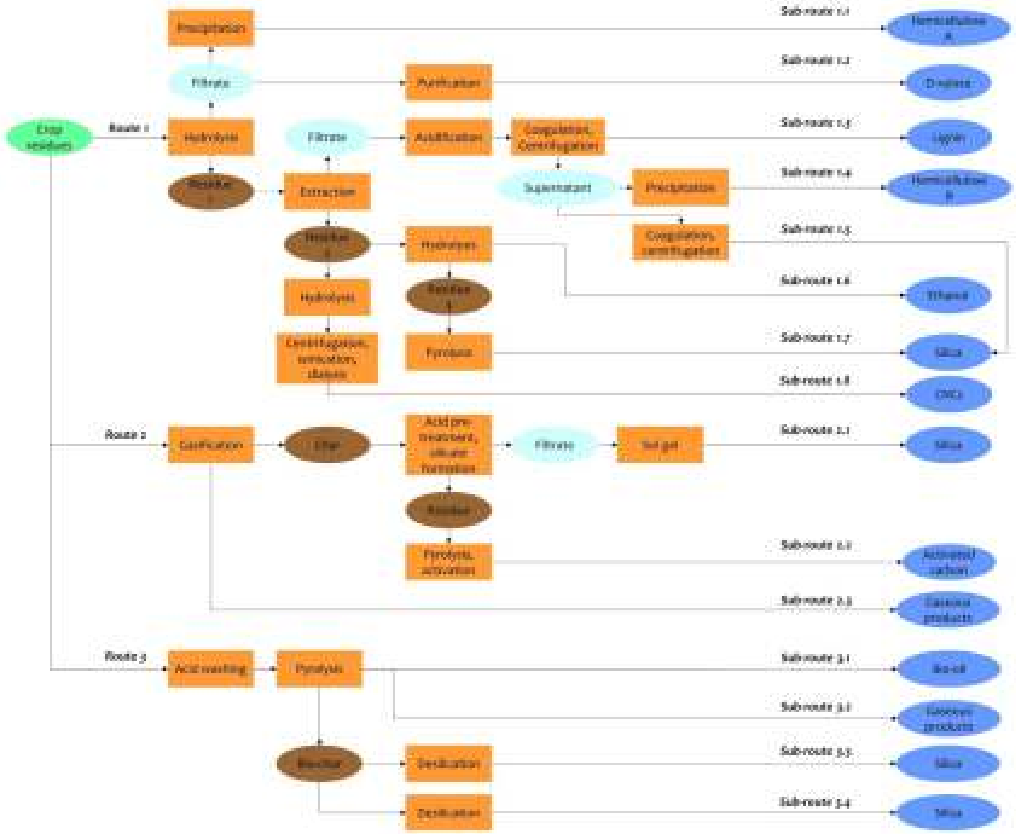

**Figure 13**. Simultaneous recovery of valuable components from crop residues, adapted from Barana et al. [28], Kauldhar et al. [91], An et al. [195], Zhang et al. [194], and Su et al. [197].

### *5.3. High energy consumption and chemical reagents in silica synthesis*

Most of mentioned methods in this study utilize high temperature process to remove major constituent of crop residues. Moreover, concentrated acids such as HCl, $H_2SO_4$, $H_3PO_4$ used in silica extraction process to remove metal alkali impurities through modest acid hydrolysis or hydrothermal. Alkali oxides such as NaOH and KOH also used to obtain silicate component as silica precursors in 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 integrated process using green reagents and novel heat sources with high efficiency. In case of metal alkali removal, milder acids such as citric acid [69, 104, 168, 169] and acetic acid [169] can be applied via chelation process to avoid dangerous residues. On other hand, laser ablation [85] and microwave irradiation [180, 181] are two techniques which can generate heat energy to decompose organic compounds of crop residues in silica extraction process with high efficiency.

## 6. Conclusion

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

1. There are three advantageous factors to determine crop residues as sustainable precursors for siliceous materials: large portion of silica in ash of crop residues, huge abundant of crop residues confirmed by global generation data of extractable silica, and high utilization of silicon fertilizer enhancing yield of production of crop residues.
2. Extraction method of silica from crop residues can be classified into four part based on their goals: (1) generating ash containing high concentration of silica (2) removing metal alkali impurities on ash (3) tailoring textural properties of silica particle, and (4) utilizing low energy processing method.
3. Crop residues-derived silica particle are widely developed on concrete materials, ceramic materials, thermal insulation purposes, adsorption of pollutants in aqueous solutions, biomedical application, catalyst for synthesizing valuable compounds, chromatography stationary phase, and ER fluid components.
4. The challenges on developing siliceous materials from crop residues are mainly related to silica depletion in soil, segregation approach on energy recovery and silica extraction, and utilization of high energy processing and chemicals.
5. Crop residues are considerable as promising silica precursors for wide applications through integrated technological process which can recover energy, lignocellulosic materials, carbonaceous materials, and of course silica, simultaneously.

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