

Review Article

Crop Residues as Potential Sustainable Source of Silica in the Era of Climate Change: A Review

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ABSTRACT

Prospecting for sustainable resources will be suitable to generate silica materials extensively used for different commercial applications. Accumulated amorphous silica which is found in the crop residues removed during the harvesting is called as phytolith. From various crop residues discussed in this study, sugarcane leaves are most important and capable source of silica. Synthesis methods are in order to generate silica particle with high processing efficiency. The applications for silica particles extracted from crop residues differ depending on their unique characteristics related to textural and morphological properties. Developing silica materials from crop residues involve several challenges involving silica depletion in croplands, separation of valuable components from crop residues, and the high use of energy and chemical reagents. Use of industrial wastes containing silica can be utilized as silicon fertilizer in crop lands facing silica depletion. An integrated approach can be applied using low energy with fewer chemical methods to retrieve energy, lignocellulosic, siliceous, carbon containing material from crop residues.

Keywords

Crop Residues,
Silica,
Climate Change

Introduction

Increase in global population enhances the sustainable production of crop plants to achieve global food demand (Josephson *et al.*, 2014). The generation of residues after harvesting will be proportional to the productivity of crop plants. High abundance of those crop residues must be handled by applying compatible technological processes to retrieve their beneficial components. Silica work as a precursor for electronic coating, ceramics, concrete, chromatography, anticorrosive agent and optical materials. The employment of high purity silica in industrial applications will be costly because its processing requires high temperature. Thus, the silica synthesis from crop residues will be

a viable option to reduce the processing costs and to deal with sustainability challenges. Crop residues are subjected to thermal, physical, chemical, or biological processes to obtain silica. Different silica materials that can be generated from crop residues are amorphous silica powder, silica nano particles, silica xerogel, silica aerogel, mesoporous silica, and microsphere silica.

Silica as a constituent in crop residue

Silica has gained high attention for agricultural practices due to its advantageous impacts for improving the yields and qualities of various crops. Those advantageous impacts are related with silica accumulation behavior which differs by plant species.

Crops like 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 considered to take up and deposit more silica by active transport (Yan *et al.*, 2018). Active transport permits more silica trans-membrane movement because of the presence of Si transporter proteins such as poly-2-vinylpyridine-1-oxide found at the plasma membrane. Figure-1 illustrates the silica uptake mechanism and its effect on agricultural plants. Silica serves as insoluble crystalline aluminosilicates in soil that cannot be taken up by root plants (Yan *et al.*, 2018). This primary silicate mineral is weathered and desilicated to release 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 (Ma *et al.*, 2015). It is then translocated into the shoot through stream transpiration by xylem. Due to large waterloss, silicic acid is concentrated and further polymerized into an amorphous silica phase without any energy higher than 2 mol L⁻¹ of concentration (Ma *et al.*, 2015). The proportions and locations of amorphous silica differ with species and age of plants. 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 (Shakoor *et al.*, 2014). Mature plants are believed to possess the largest portion of deposited amorphous silica because of the irreversible silica deposition process in older cellwalls. The SiO₂ content in crop residues varies in the range of 9–93%. Some dicots are categorized as intermediate Si-accumulating plants such as groundnut, mustard, and rapeseed, show less SiO₂ content. Crop residues from monocots such as barley, corn, oat, rice, sorghum, and wheat tend to contain high silica concentrations because of their active

silica uptake. Silica is more concentrated in pericarp cells as compared to stem cells, since the beneficial effect of silica in providing a physical defense by creating a stiff structure in seeds or grains.

Different crop residues and their silica content

Rice crop residues are highly siliceous. Silica rich plant material has the potential of change the electrochemical properties of acidic soils that reduces P fixation; enhances base retention and increase the soil pH. Therefore, retention or incorporation of particularly the rice residues can exhibit all the benefits of liming acidic soils. This is a common practice with most Indian farmers in the hills where pH of the soil is less. Silicates and organics (rice straw) improve the net negative charge, neutralizes acidity/detoxification of Al through changing soil pH and point of zero charge of soil sediments having changeable charge contributing materials; reduce P-fixation and increase Si content in plants.

Rice straw and rice husk possess 76 g silica/kg crop and 40 g silica/kg crop respectively. They possess highest silica yield. By keeping in mind those values and the global production of rice, the value of extractable silica from rice straw and rice husk is 28,000–55,000 million kilograms per year. Sugar cane leaf has less silica yield than rice straw and rice husk but high productivity of sugarcane can enhance adequate extractable silica at approximately 37,000 million kilograms per year. Sugarcane leaf will be the best agricultural residue for generating silica if harvested area will be considered. It can generate 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 comparatively lower silica yield.

Generally, the straw residues provide high yield and productivity than that of husks. For example, the wheat straw generates up to 34 g silica per kg crop which is higher as compared to wheat husk with approximately 3 g silica kg crop of yield. The amount of extractable silica and productivity will be proportional to ash ratio in crop residues. Hence, crop residues with higher ash content will provide higher sustainability of silica production. Figure-1 presents the data plots for yield and productivity. For classifying different types of crop residues as a silica source. Class I consist of crop residues with high residue ratio as well as ash content which can generate high yield and productivity. Rice straw, rice husk, sugarcane leaf, wheat straw, and oil palm husk are classified as Class I 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. Crop residues with less 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.

Rice husk as a source of silica

Rice husk is a by-product obtained from rice milling industries and it represents 20% of the weight of the rice (Ang *et al.*, 2012). The major inorganic constituent in rice husk is silica (~20%) (Rohatgi *et al.*, 1987). The trend of extraction of silica from rice husk is increasing in the field of current research. Most of the rice husk is treated only as waste and disposed to landfill, but this waste can create a fire and environmental pollution. Moreover, particles originating from burning rice husks can cause respiratory diseases if

inhaled (Vaibhav *et al.*, 2014). Therefore, recycling waste and recreating it into a high-value material are important in order to maintain environmental sustainability. Rice husk can be utilized as a raw material for the production of products using silica because of high silica content (Gu *et al.*, 2013).

Rice straw as a source of silica

Rice straw is the stem of rice plants that are sorted out during the rice harvest and are considered as agricultural waste. Rice straw available in large quantities and does not have a commercial use due to lack of awareness (Zaky *et al.*, 2008). Rice straw is one of the agricultural waste that has high silica content (Agbagla-Dohnani *et al.*, 2001; Hessien *et al.*, 2009). The content of silica in the rice straw is more than other plants. Organic components present in rice straw is cellulose (32-47%), hemicellulose (19-27 %), lignin (5-24 %), and ash (13-20 %) (Santos *et al.*, 2010). Ash constituents depend on the variety of rice, climatic, and agroclimatic conditions where rice is cultivated (Zaky *et al.*, 2008).

Bagasse as a source of silica

Bagasse is one agricultural wastes that contains silica. Silica nanoparticles can be produced from agricultural waste, in which one of them is bagasse. (Vaibhav *et al.*, 2014) The method used is dissolution by alkaline NaOH and precipitation by sulphuric acid.

Corn cobs as a source of silica

Corn cobs are an agricultural waste obtained from corn. Corn cobs consist of more than 60 % silica with less amounts of metal (Adesanya and Raheem, 2009). Corn cobs can be used as an economical raw material in silica production. Ash corn cob is obtained after combustion so that it does not need

further grinding, and corn cob ash is the most economical source of silica (Velmurugan *et al.* 2015).

Method for extracting silica from agricultural waste

There are mainly three methods for producing silica from agricultural waste, i.e. chemical treatment, thermal treatment, and microbial treatment (Fadhulloh *et al.*, 2014). The first stage is done in the acid leaching (Adam *et al.*, 2008; Adam *et al.*, 2011; Ding and Su, 2012; Li *et al.*, 2011; Anget *et al.*, 2012; Zulkifli *et al.*, 2012; Guet *et al.*, 2013; Noushad *et al.*, 2014; Kongmanklang and Rangsriwatananon, 2015; Kumar *et al.*, 2015). Acid leaching of agricultural waste is utilized to wipe out impurities and improve the purity of the silica contained in that. Organic compounds in agricultural waste and different impurities can be changed over into ions dissolved by a normal acid treatment (Vaibhav *et al.*, 2014).

Chakraverty *et al.*, (1988) reported the effects of acids in eliminating metal impurities from rice husk by comparing the different levels of metal impurities which were not treated with acid as well as treated with HCl, H₂SO₄, and HNO₃. The rice husks that were not treated metal levels have very high of sodium, potassium and calcium as compared to ferrous metals, magnesium, manganese, zinc, and copper. Interestingly, the rice husks which were treated with acid, metal levels declined.

Rafiee *et al.*, (2012) reported the HCl in the stages of acid leaching can effectively done at concentration of 1 M for removal of metal with a surface area and the pore volume generated is likewise acceptable. The production of mastoid SiO₂ with various crystal structures with other SiO₂ crystal (Ding & Su, 2012). In that, the first stage is

purification with acid and alkaline pre-treatment to remove the metals Na, Mg, Ca, Mn, Al, Fe, Zn, and other elements with acidic water (consisting of 30 % H₂O₂ and 10 % HCl) as well as to remove the metals Na, Cl, P, S, and other elements with alkaline water (consisting of 30 % NH₃.H₂O). The purified rice husks are firstly washed and then heated at a temperature of 600⁰C for 10 hours to obtain a white silica product which can be obtained by ultrasonic fragmentation method. However, the use of strong acids in acid leaching has negative impacts to the environment and also cause economical problems because the price of acid is also expensive.

Therefore, other experiments using acids which are environmentally friendly, harmless, and more economical like by using a carboxylic acid (citric acid) and hydrolysis process at temperatures above 200⁰C to produce silica with a purity of 99% (Umeda and Kondoh, 2008). Metal impurities such as Na, K, Ca, Mg, Fe, and Cu can be excluded from rice husk through a chelate reaction between the carboxyl group (-COOH) to metal.

Real *et al.*, (1996) stated that the process of acid leaching in rice husks before burning, produce silica powder with a large surface area. Estevez *et al.*, (2009) suggested a method to remove silica particles in the rice husk through microbial fermentation using fungi and worms.

Effects of silicon fertilizer

Silicon is a beneficial plant nutrient that provide protection from biotic (pests and diseases) and abiotic stresses. The tolerance against pests and diseases is due to the interaction between the host and the pathogen related to the presence of silicon along with a certain defensive response by plants. Silicon

deposition in plants improves the abrasiveness of the plant tissues that prevent herbivores and arthropods from digesting plant bodies rich in silicon (Snehal *et al.*, 2018). Abiotic stress resistance is defined as the ability to exert resistance to unfavorable conditions mainly due to extreme climate changes. This is provided by deposited silica mechanical 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, and reduce chaffing of grain (Shakoor *et al.*, 2014). Increase in food production is crucial in order to maintain global food security. Silicate fertilizer in place of additional macronutrients can also be applied to enhance the productivity of many agricultural plants. Once agricultural productivity increases, the generation of residues also increases by enhancing extractable silica. Figure-2 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 due to the reason that many crop like rice, wheat, and sugarcane categorized as highly Si-responsive plants with large Si demand (Yan *et al.*, 2018). The generation of extractable silica must be estimated as much as crop production to procure a larger amount of silica from crop residues. For instance, Sun *et al.*, (2019) reported that silicon fertilizer application with maximum dosage in silicon enriched soil increased the rice phytolith content by 32.83%, 27.01% and 32.06% in stem, sheath and leaf respectively.

Recent progress on silica material applications derived from crop residues

Concrete mechanical performance is reported to be improved by the presence of amorphous

silica particles derived from crop residues as partial replacement for ordinary concrete materials. Amin *et al.*, (2019) 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 be mixed with other materials in order to partially replace cement in concrete fabrication. Pandey and Kumar (2019) mixed rice straw silica along with commercial micro-silica as partial replacement for Ordinary Portland Cement (OPC) to enhance the mechanical strength of Pavement Quality Concrete (PQC). Highest compressive, flexural and tensile strength was obtained when OPC was partially replaced by 5%–7.5% rice straw silica and microsilica composite. Sorghum husk ash was mixed with Laterite to partially replace Ordinary Portland Cement (OPC) up to 20% in concrete construction (Williams *et al.*, 2014).

Refractory ceramic materials

Crystallization process at temperatures higher than melting point of crop residues produce silica crystal phase like quartz, cristobalite, tridymite, etc. Fernandes *et al.*, (2017) reported that thermal treatment at 1000 °C will be economical to obtain silica with cristobalite and tridymite crystalline phases. These silica crystals are useful components for preparing refractory ceramics. Furthermore, silica particles can also be incorporated with other ceramic reinforcement materials in various aluminum matrix forms to achieve good strength and ductility combinations (Pattnayak *et al.*, 2018). Several studies were carried out to know the possibility of using silica obtained from crop residues in fabricating refractory ceramics through replacement of kaolin clay. Sobrosa *et al.*, (2017) developed refractory ceramic materials by replacing kaolin clay with rice husk silica at various percentages of

volume. The use of 10% silica resulted in enhanced mechanical strength without decrease in the thermal shock strength. The rice husk silica impact on the mechanical and thermal properties of refractory ceramic materials was studied by Stochero *et al.*, (2017) Refractory ceramics are fabricated through replacement of kaolin clay with 20% rice husk silica and various volume percentages of steel fibers. The results suggest that considerable improvement in the mechanical and thermal properties of refractory ceramics can be obtained through replacement of kaolin clay with rice husk silica and steel fibers. Studies were conducted to fabricate glass–ceramic tiles using rice husk as silica precursors. Glass–ceramic tiles were successfully developed by Andreola *et al.*, (2013) using a sinter-crystallization process at 900 °C using a glassy frit formulated in the MgO–Al₂O₃–SiO₂ composition system. Those ceramic materials show higher bending strength and Mohs hardness as compared to commercial glass–ceramics.

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 controlled using silica materials generated from crop residues. Silica powder and silica gel obtained from rice husk ash are successfully used to prepare polymers and grafted copolymers for the adsorption of gadolinium (Gad *et al.*, 2017). This result shows that silica gel grafted copolymer have maximum Gd (III) adsorption capacity of 229.36 mg/g which is more than the other adsorbent used in Gd (III) adsorption in other works. Another study by Hasan *et al.*, (2019) prepared low-cost fibrous silica KCC-1 obtained from rice husk ash for Pb(II) removal. The adsorption–desorption

analysis indicates that KCC-1 is economical as a good adsorbent for removing Pb (II) from aqueous solutions. This is shown 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 obtained from rice husk has good adsorption capacity for removing ciprofloxacin drug from aqueous media (Nasaar *et al.*, 2019). That silica Nano-particles show highest ciprofloxacin adsorption capacity at 190 mg/g is much higher as compared to commercial silica gel (11.0 mg/g) under the same optimum conditions.

Catalyst applications

The application of silica particles obtained from crop residues in catalyst synthesis generate valuable compounds have been widely investigated. Salakhum *et al.*, (2018) 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.*, (2019) synthesized Nano acid catalyst derived from rice husk silica for the synthesis of 3,4-Dihydropyrimidinones/thiones compounds. This Nanocatalyst 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 Miguez *et al.*, (2018). 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 (Ghime *et al.*, 2017) and organic dyes (Vu *et al.*, 2019). The silica mesoporous structure which provides sufficientcavities and surface area, creating more active sites for targeted compounds. The distinct dye degradation mechanism was carried out using carbon-containing SiO₂-based photocatalysts 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 (de Cordoba *et al.*, 2019). A similar adsorption mechanism was also obtained by Velmurugan *et al.*, (2015) when amorphous silica from corn cobs were utilize 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.

Fig.1 Prospecting crop residues based on their silica yield and global silica productivity (Wahyu *et al.*, 2020)

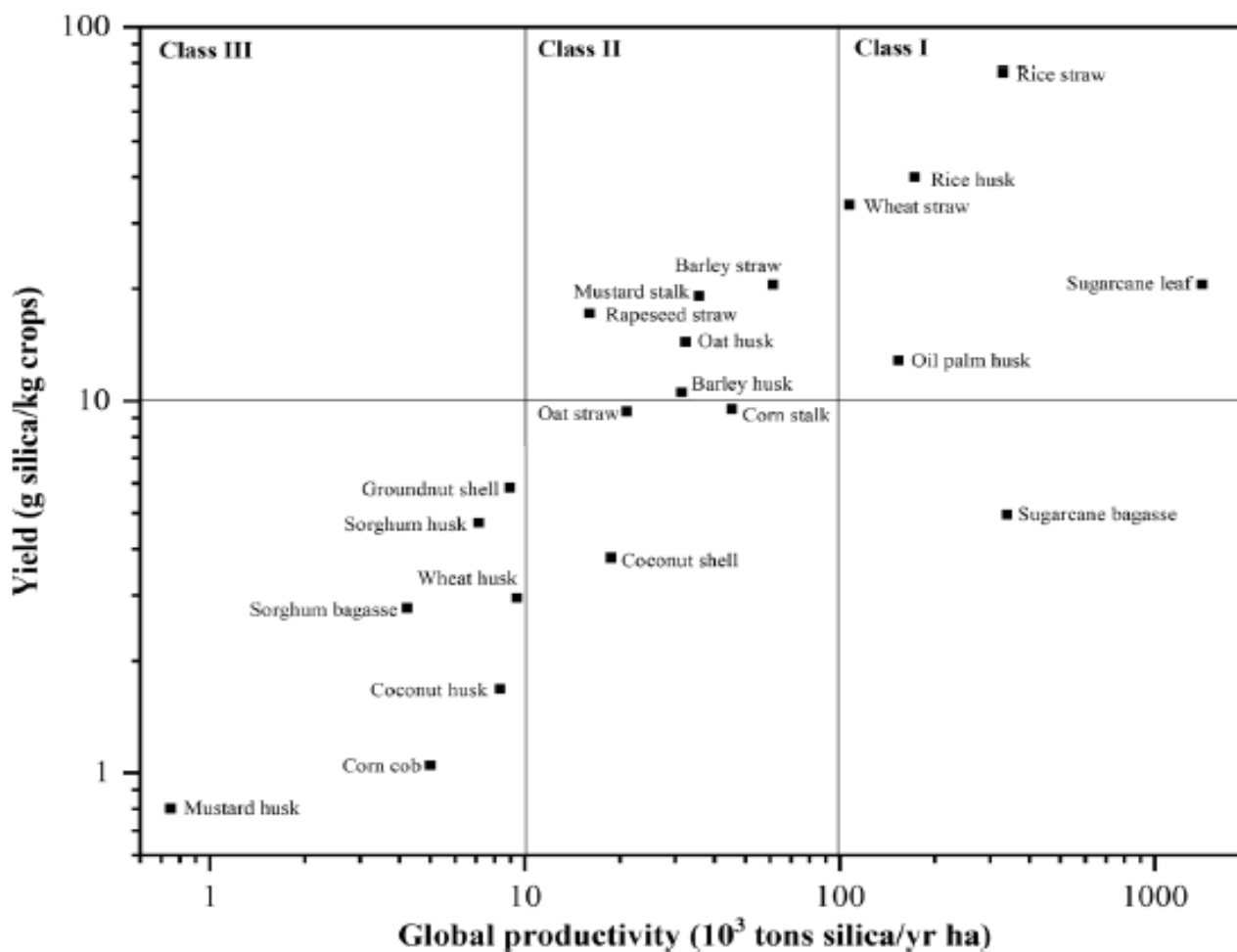


Fig.2 Crop residue enhancement generation using blast furnaceslag and potassium silicate field fertilization (Yan *et al.*, 2018)

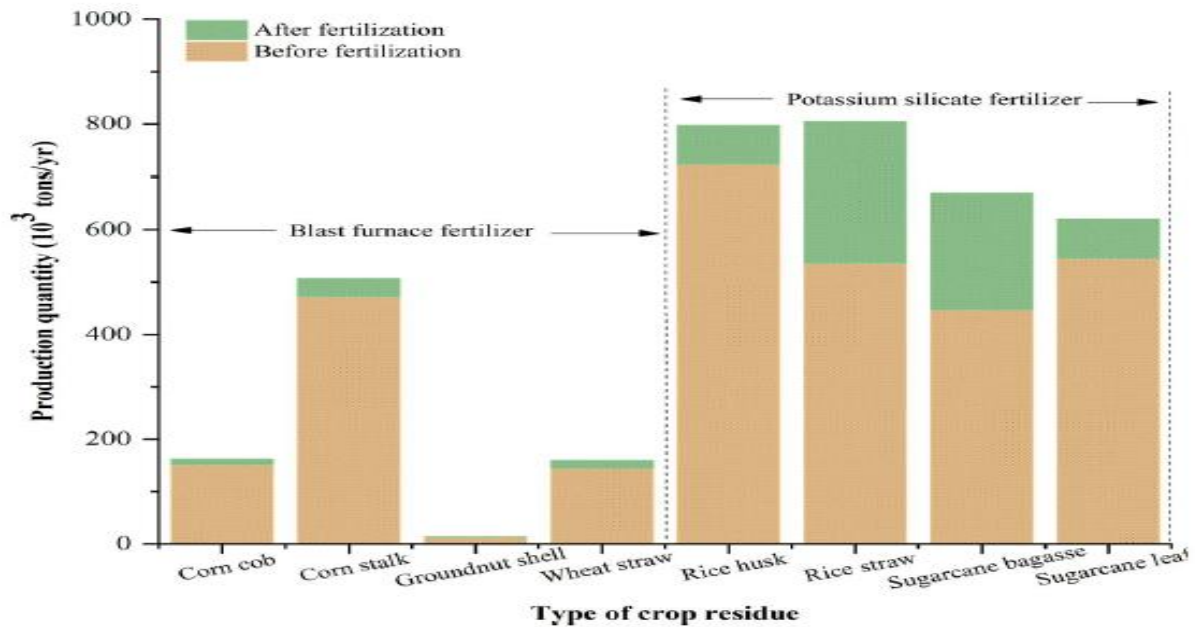
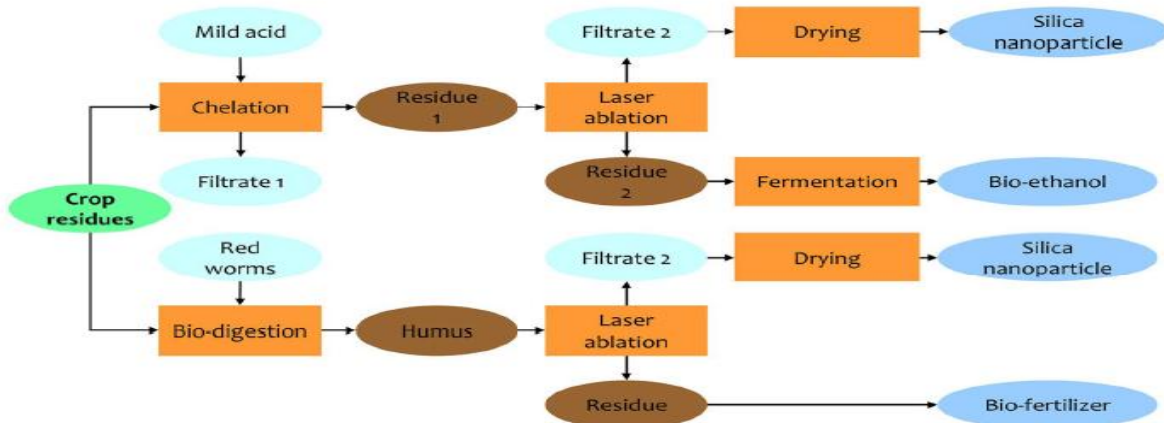


Fig.3 The proposed green technologies for recovering silica from crop residues, adapted from San *et al.*, (2014), Estevez *et al.*, (2009), and Torres *et al.*, (2017)



Other applications

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.*, (2013) 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 (Zou *et al.*, 2013), waste silicon sludge (Ding, *et al.*, 2015), silicon kerf waste (Han *et al.*, 2020), waste products from the phosphate fertilizer industry (Elineema *et al.*, 2013) may also be considered as fertilizer-Si sources.

Development of green technology for recovering silica from crop residues

Most of the methods mentioned in this study involves a high temperature process in order to remove the major constituents from crop residues. Concentrated acids such as HCl, H₂SO₄, H₃PO₄ are utilized in the silica extraction process to remove metal alkali impurities. Alkali oxides like NaOH and KOH are also used to obtain silicate components such as silica precursors by sol gel method. The utilization of chemical reagents may generate hazardous liquid residues which are harmful for biotic components. This issue can be solved by using an integrated process using green reagents and high efficiency sources of heat. Milder acids such as citric acid and acetic acid can be applied through the chelation process to remove metal alkali and prohibit accumulation of dangerous residues. Laser ablation and bio-digestion 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. 3.

In conclusion, the crop residues as economical silica precursors are strongly related with their high silica ratio, global productivity, and the effect of silicate fertilizer on crop production. The silica extraction method from crop residues can be classified into three levels:

Obtaining high purity amorphous silica.
Customizing the morphological and textural properties of silica nano-particles.
To find out a high efficiency process for generating silica nano-particles.

The structure, particle size, and textural properties of silica particles obtained from crop residues will influence their further application. Silica nano-particles with good textural properties have received more attention in various application in concrete materials, ceramic materials, thermal insulation purposes, adsorption of pollutants in aqueous solutions, biomedical applications, and catalysts for synthesizing valuable compounds, chromatography stationary phase, and algae culture growth. The challenges in evolving siliceous materials from crop residues are mainly associated with silica depletion in soil, segregation approach to energy recovery and silica extraction, and the evolution of green technologies. Crop residues are promising silica precursors for different applications through integrated green technological processes that can recover energy, lignocellulosic materials, carbonaceous materials, and of course silica, simultaneously.

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