Biomass as a sustainable resource for value-added modern materials: a review

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Abstract: Over the past century, the world’s population has increased greatly. The growth in the population has increased the global food demand, so the food sector has increased its production. As a result of the increased production and consumption, a huge amount of agro-food waste is being generated yearly. Rice husk, wheat straw, sugarcane bagasse, corn husk, peanut shell, eggshell, are just a few examples of agro-food wastes. As these agro-food wastes and their by-products are left unused and unattended, their amount is increasing globally. It is imperative to find ways to put these wastes to environmentally viable use. These wastes find direct uses in biofertilizers, mud houses, animal feed, biofuel, and heat generation in small-scale industries, etc. After heat generation, ashes are considered as a secondary by-product, which can be used as a sustainable and renewable resource for synthesizing value-added products for various applications. This article presents a review of the traditional and advanced methods of utilizing these wastes in household applications, animal feed, fertilizers, fuel generation, pyrolysis, and for the removal of toxic metals from polluted water. These secondary resources can also be used in construction materials and for the synthesis of glasses and glass–ceramics, which can be used in bioengineering, optical, and dielectric materials. Agro-food wastes can be used as resource materials to develop modern materials with better properties instead of using minerals. This not only reduces the environment- and management-related problem of the wastes but also provides a sustainable alternative way to produce cost-effective value-added materials for the benefit of society. © 2020 Society of Chemical Industry and John Wiley & Sons, Ltd

Keywords: agricultural and food wastes; construction and cement; glasses and glass ceramics; photoluminescence; dielectric constant; microelectronics; bioactive materials

Introduction

All across the globe, large amounts of waste are being piled up at a rate that is increasing each year. In 2016, 2.01 billion tonnes of solid waste was generated, amounting to a footprint of 0.79 kg per person per day. In India alone, about 960 million tons of solid waste are being generated annually by the industrial, mining, municipal, agricultural, and other sectors. Of this, ~350 million tonnes is organic waste from the agriculture sector; ~290 million tonnes is the inorganic waste of industrial and mining sectors, and ~4.5 million tonnes is...
hazardous. Figure 1 shows different types of waste being generated.

A growing population, growing economies, and industrialization are some of the causes behind the enormous amount of waste being generated. Waste management has become a growing concern for many countries. As a result of the rapidly growing world population and urbanization, food demands have multiplied many times. The agricultural sector therefore has to increase its output, and a large amount of agro-food waste is being generated each year. The most commonly produced agro-food wastes are rice husk (RH), sugarcane leaves (SCL), sugarcane bagasse (SCB), corn husk (CH), barley husk (BH), eggshell (ES), coconut cell (CC), peanut shell (PS), and wheat straw (WS) residues, etc.

Agricultural waste is biodegradable and eco-friendly but, in some cases, the degradation process is prolonged and lengthy. Farmers want their fields to be free from the previous crop residue as soon as possible to prepare them for the next crop season. Due to the high cost of other waste-management methods, some farmers opt to burn the crop residues in open fields, which creates environmental pollution. It is fast becoming urgent to find more viable and environment-friendly solutions to manage these wastes. These agricultural and food wastes are conventionally used in a few applications like animal feed and mud houses, and for energy generation in small-scale industries such as sugar mills or rice mills as shown in Fig. 2.

Currently, much effort is being devoted to developing renewable biomass fuels such as bioethanol, biogas, and biodiesel, from agro-food wastes. It is imperative to know the chemical and physical properties of agro-food wastes to find their use in appropriate applications. Eggshell and rice-husk ash (RHA) contain high levels of calcium carbonate and silica, respectively, and hence can be used for applications that require high calcium and silica content, such as calcium silicate glass, $\text{Ca}_2\text{SiO}_4$ phase acts as host materials for making white-light-emitting diodes, and calcium generation sources for animals. In addition to this, properties like surface area, and small particle size are important in applications like wastewater treatment, and the degradation of organic dyes. Some characteristics (compositions, particle sizes, bulk density, calorific values, etc.) of agro-food wastes like RH, SCL, SCB, WS, PS, CH, CC, and ES are given in Table 1.

Furthermore, these agricultural wastes are being used to make biocomposites and other biofertilizers to enhance the fertility of the land. It has been found that composted RH, dry SCL, etc., can help to improve the growth of plants as they increase soil fertility by improving the organic content. Bio-fertilizers can enhance the availability of organic substances to the plants. This environment-friendly approach also offers an alternative to the hazardous chemical fertilizers.

Another possible application of agriculture waste is to produce silicon from RH, which contains around 80–90% silica. Pure silicon nanoparticles can also be synthesized, and can be used in Li-ion battery anodes. Kavitha et al. found that direct pyrolysis of RH can produce SiC, which has many applications because of the low coefficient of thermal expansion (CTE), oxidation resistance and excellent abrasion / wear resistance. A review by Adebisi et al. highlights the importance of using agriculture wastes to produce nanosized solar grade silicon, which involves lower cost than conventional methods.
Engineering applications of biomass derived materials

It is also possible to use agriculture wastes as biosorbents for the removal of toxic heavy metal ions from aqueous solutions. Another novel approach is to incorporate raw rice husk and foam bubbles in magnesium oxysulfate cement paste to develop lightweight building materials. They can also find use as the inner partition walls and thermal insulating components of the buildings.

Even if agro-food wastes are utilized in the above ways, ashes are generated as second-generation by-products in the developing countries. These wastes are often not disposed of properly; instead, they are dumped on open ground. Ashes are harmful to all living beings due to their small particle size. Thus, environment-friendly and cost-effective methods are required to manage the ashes of agro-food wastes. Usually, these ashes contain a large amount of silica, calcium oxide, potassium oxide, sodium oxide, and some other trace element oxides. These renewable resources can be converted into value-added engineering materials using different chemical, physical, and mechanical methods. Due to the high silica content, some agro-food waste ashes are used in civil construction. Currently, these ashes are being used as resource materials to produce glasses and glass ceramics with widespread applications. For instance, RHA is now being studied for its possible use in water treatment, brick manufacture, light-emitting diode (LED) applications, etc. On the other hand, food wastes are being explored for use in tissue-engineering applications, enhancing soil quality, synthesizing environment-friendly catalysts, biodiesel production, etc. Many research groups have been exploring methods for the effective utilization of agro-food wastes for several potential applications.

Apart from conventional applications of agro-food wastes, the effective use of second-generation agro-food waste ashes would not only improve the financial condition of the farmers but would also pave the way for meaningful solutions and management of these harmful ashes. There is scope for a lot of progress in this field, as the influence of trace elements, inherently present in agro-food waste has not been very widely explored. It is expected that due to the presence of certain transition metal oxides in trace amounts in the agro-food waste ashes, these could be used as resource materials for synthesizing optically active materials. Some of these trace elements can also act as phase stabilizers.

A large amount of agro-food waste being generated thus finds use in various applications. The second-generation ash left behind creates a disposal and pollution problem. Hence, it is important to find appropriate ways to utilize these waste ashes too. As rice and eggs are the staple food of a large population around the world, these constitute a large portion of the global agro-food waste content. On the other hand, WS, dry SCL, groundnut shell, CC, CH, and BH are region-specific wastes but are common in large parts of the world. So, in the present review, the emphasis is only on the common agro-food wastes like RH, ES, SCL, WS, CH, PS, and their applications. The aim of the present study is to provide updated information about the agro-food wastes and their application in producing different value-added cost-effective materials. This review article is an attempt to present a comprehensive and systematic overview of the various ways in which the agro-food wastes and the second-generation problematic ashes can be used directly. Initially, we summarized the use of eggshell in biomaterials and as an adsorbent of heavy metals. In the subsequent sections, the conventional and modern applications of agro wastes are discussed, followed by their use as renewable resource materials for possible applications in civil, optical, dielectrics, and the bioengineering field.
Utilization of eggshell waste

Eggshell contains a very large amount of CaCO₃ along with some trace elements.⁷⁴ These days, ES is being used for many applications, either directly or after chemical treatment. It is commonly used as an adsorbent for the removal of hazardous pollutants. Wastewater containing dyes poses a huge problem because their elimination is difficult due to their high solubility in water. Tsai et al.¹⁷ studied the potential of calcified ES (CES) and its ground eggshell powder (ESP) for the adsorption of cationic basic blue 9 and anionic acid orange 51 from aqueous solution by varying the agitation speed, initial dye concentration, adsorbent mass and temperature. It was concluded that ES waste could be used as an adsorbent for the removal of anionic dye. Further, Abdel-Khalek et al.⁷⁴ found that industrial waste ES could be used as an adsorbent for methylene blue (MB) and Congo red dyes. The effect of ES in binding three different dyes, methylene blue, bromphenol blue, and methyl orange from their aqueous solutions has also been studied.⁷⁶ It has been concluded that ES can act as an effective adsorbent for removing anionic and cationic dyes. Some modifications have been made to the ES surface to improve its performance as an adsorbent. Akazdam et al.⁷⁷ used ES treated with NaOH to study its effectiveness as an adsorbent for MB and acid orange 7. It was found that around 75% MB could be removed using NaOH treated ES. El-Kemary et al.⁷⁸ modified the calcined eggshell (CES) by depositing sol–gel titanium dioxide nanoparticles and obtained a novel hybrid nano-biosorbent, namely TiO₂–CES. It was concluded that TiO₂–CES could be used for the absorption of acid red nylon 57 dye from aqueous solution. The experiments showed that a low adsorbent dosage was enough for removal of 99.89% of dyes. Table 2 gives the values of adsorption capacity of different dyes obtained using ES as an adsorbent.

It has also been found that ES can be used for removal of toxic heavy metals from water. Jai et al.⁸⁰ used CES for the removal of heavy metals like Cd, Cr, and Pb from wastewater. It was concluded that CES results in complete removal of Cd, as well as 99% removal of Cr. Numerous studies, have indicated that ES can be useful in the removal of Pb from water and soil.⁸¹–⁸³ The feasibility of eggshell membrane (ESM) for the removal of Cr⁶⁺ ions from the aqueous solution has also been reported.⁸⁴ Under optimum conditions, maximum removal of 81.47% has been achieved. Angelis et al.⁸⁵ synthesized the hydroxyapatite from eggshell waste and studied its potential as an adsorbent for Ni⁵⁺ removal from its aqueous solution. It was found that the maximum adsorption capacity was higher than that from the other waste-derived adsorbents.

It has also been reported that the consumption of water with a high boron content can be harmful to living beings.⁸⁶ Al-Ghouti and Khan⁷⁷ found that eggshell membrane (ESM) can adsorb 97% of boron; hence, it can be used as an adsorbent for the removal of boron from water. Zhang et al.⁸⁸ utilized ESM as solid-phase extraction adsorbent for the removal of As⁵⁺. It was found that, under optimal conditions, ESM was able to extract As⁵⁺ with the highest adsorption capacity of 3.9 μg⁻¹. Chen et al.⁸⁹ investigated the esterification of carboxylic groups on ESM with methanol. The results suggested that the arsenate sorption capacity of methyl esterified eggshell membrane (MESM) was 200 times better than that of bare ES. Further, ES was also used for the removal of Cu and Hg.⁹⁰,⁹¹ Table 3 gives the adsorption capacity of eggshell for different dyes from the wastewater.

Some studies have shown that phosphate is a toxic inorganic pollutant; high concentrations of phosphate can lead to severe damage in the human body.⁹² Panagiotou et al.⁹³ used CES for the removal of phosphorus from wastewater and leach liquid from anaerobic sludge. It was concluded that CES could act as useful material for phosphorus removal.

Muliwa et al.⁹⁴ studied the efficiency of the use of ES waste in the pre-treatment and neutralization of highly acidic and contaminated acid mine drainage (AMD) leachate from coal mine dumps. The results indicated that ES waste could act as an efficient and inexpensive material in the pre-treatment of AMD polluted sites.

It has been found that polycyclic aromatic hydrocarbons (PAHs) are carcinogenic and can cause cardiovascular diseases in humans. Wang et al.⁹⁵ demonstrated that ESM templating of the mixed hemimicelle / admicelle of linear alkylbenzenesulfonates (LAS) could act as an adsorbent for the enrichment of PAHs in aqueous samples. This method

Table 2. Comparison of the adsorption capacity of eggshell for different dyes.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Dye</th>
<th>Adsorption capacity (qe) (mg g⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eggshell + Eggshell membrane</td>
<td>Methylene blue</td>
<td>94.9</td>
<td>⁷⁹</td>
</tr>
<tr>
<td></td>
<td>Congo red</td>
<td>49.5</td>
<td></td>
</tr>
<tr>
<td>Eggshell powder</td>
<td>Acid orange 51</td>
<td>112.36</td>
<td>¹⁷</td>
</tr>
<tr>
<td>Eggshell membrane</td>
<td>Methylene blue</td>
<td>3.86</td>
<td>⁷⁶</td>
</tr>
<tr>
<td>NaOH treated eggshell</td>
<td>Methylene blue</td>
<td>66.67</td>
<td>⁷⁷</td>
</tr>
<tr>
<td>TiO₂-Calcined eggshell</td>
<td>Acid red nylon 57</td>
<td>18.8</td>
<td>⁷⁸</td>
</tr>
</tbody>
</table>
gave satisfactory results in the detection of PAHs in water samples. Pharmaceuticals are another major water pollutant whose increased concentration in the water poses a huge problem. Pavlovic et al.\textsuperscript{97} studied the suitability of ES as a sorbent for the removal of five pharmaceuticals: dexamethasone (DEX), febantel (FEB), praziquantel (PRAZ), procaine (PROC), and tylosin (TYL) from water. It was found that ES could act as cost-effective biosorbents for the removal of the pollutants from water.

In addition to the above-mentioned applications, ES treated powder can be directly used as a coating material on the body of implants to generate hydroxyapatite (HA) layer.\textsuperscript{98} In the case of implants, a bioactive coating material is normally used to protect the substrate surface. The direct use of substrate may cause undesirable reactions and ill effects on the body.\textsuperscript{99} So, plasma spraying method is most widely used for coating on metallic implant devices of HA developed from wastes.\textsuperscript{100} The dissolution rate of HA coating is also correlated with the biochemical calcium phosphate (CaP) phase of the coating; more crystalline HA will be more resistant to dissolution in the human body. If the dissolution rate is faster than bone growth or implant stabilization, coating would be useless.\textsuperscript{101} Studies have suggested that both amorphous and crystalline phases in are desirable in coating materials to promote a more stable interface with the biological environment.\textsuperscript{102} Eggshell powder and seashell powders have been used as coating materials on Teflon and nylon substrate by using plasma spray deposition.\textsuperscript{99,103} These food-derived coating materials are naturally bioactive and biocompatible. Polymers (Teflon and nylon) have also been used for implantation purposes due to their better corrosion resistance, better mechanical properties, and better wear resistance.\textsuperscript{104} Ostrich ES find use in the fabrication of zinc calcium phosphate coatings on titanium surface by using two-step thermo-chemical deposition methods.\textsuperscript{105} This method efficiently produced zinc brushite coating after the fabrication of zinc HA, which also showed bioactivity with the precipitation of bone-like appetite precipitation of bone-like appetite, as discussed in subsequent sections.

### Direct utilization of agro-wastes

#### Animal feed

Most of the farmers use agricultural wastes to make animal feed, compost, vermin compost, mulching material, biogas, and animal shelter.\textsuperscript{106} Agro-food wastes can be directly fed to animals because of the nutrients present in these wastes.\textsuperscript{108–110} Husk and pods of common pulses with leaves and tender stems can be used as cattle feed as they are a good source of digestible protein.\textsuperscript{110} A large portion of the barley is used in the animal feed industries in many developing countries.\textsuperscript{111} Dotaniya et al.\textsuperscript{112} reported that SCB waste is consumed as cattle food, due to the presence of large fractions of fermentable sugars. Ajila et al.\textsuperscript{113} have given an in-depth analysis of the bioprocessing of agro-food wastes like rice bran. It can be used for feeding animals due to the high amount of vitamin B complex. Further, a small portion is used for the production of biofertilizers, composites, fuel and heat generation in sugar mill plants, small-scale industries, etc.

#### Bio-fertilizers

Bio-fertilizers provide a larger amount of nutrition elements to the plants, in comparison to the ordinary organic fertilizers.\textsuperscript{114} The agro-waste products – wheat bran, mustard oil cake, cicerbrown husk, peanut shell, and tea waste – have been composted to form biodegradable value-added products like biofertilizers.\textsuperscript{48,115} Biofertilizers are better than organic fertilizers as they help in maintaining the fertility of the soil, hence less irrigation water is required to increase productivity. They enrich the nutrient quality.

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**Table 3. Adsorption capacity of eggshell for various toxic heavy metals.**

<table>
<thead>
<tr>
<th>Heavy metal</th>
<th>Adsorbent</th>
<th>Adsorption percentage</th>
<th>Optimum conditions</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>C Cd</td>
<td>Calcined ES</td>
<td>100</td>
<td>After 10 min</td>
<td>80</td>
</tr>
<tr>
<td>C Cr</td>
<td>Calcined ES</td>
<td>99</td>
<td>After 10 min</td>
<td></td>
</tr>
<tr>
<td>P Pb</td>
<td>Natural ES</td>
<td>100</td>
<td>After 40 min</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>Natural duck ES</td>
<td>79.18</td>
<td>Initial concentration: 0.349 mg L(^{-1}), pH: 6</td>
<td>92</td>
</tr>
<tr>
<td>Cr(Vi)</td>
<td>ESM</td>
<td>81.47</td>
<td>Temperature: 20 °C, pH: 3.54, Cr(Vi) ion concentration: 5.0 mg L(^{-1}), time: 117.52 min, dosage 3.78 g</td>
<td>84</td>
</tr>
<tr>
<td>As</td>
<td>MESM</td>
<td>100</td>
<td>As concentration: 2 μg L(^{-1}), pH: 6</td>
<td>89</td>
</tr>
<tr>
<td>Hg</td>
<td>Thiol-functionalized ESM</td>
<td>96</td>
<td>pH: 2–8</td>
<td>91</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>ES</td>
<td>−100</td>
<td>pH: 7, agitation rate 350rpm</td>
<td>90</td>
</tr>
</tbody>
</table>

of the soil and transform organic matter into nutrients that can be used to make plants healthy and productive. They are usually prepared as carrier-based inoculants containing effective microorganisms. Several kinds of agro-wastes, such as rice straw compost, are good carrier materials for the inoculants. The biodegradation of such materials to simple sugars provides energy sources for heterotrophic microorganisms such as P-solubilizing and nitrogen-fixing bacteria. The main inoculants are bacteria, fungi, and cyanobacteria (blue-green algae). These microbes have various abilities, which can be exploited for better farming practices. Some of them help to combat diseases and some have the ability to degrade soil complex compounds into simpler forms, which are utilized by the plants for their growth. They are extremely beneficial in enriching the soil by producing organic nutrients for the soil and in converting insoluble phosphates to a form accessible to the plants for increasing plant yields. The use of microbial products as biofertilizing agents is not considered harmful to ecological processes or the environment. Beneficial effects of microbial inoculation as biofertilizers have been described by many authors. The idea of controlling and manipulating soil microflora using microbial inoculants, organic amendments and cultural management practices to create a more favorable soil involvement for optimum crop production and protection has been implemented continuously.

Biochar significantly increases the efficiency of, and reduces the need for, traditional chemical fertilizers, while greatly enhancing crop yields. Sugarcane bagasse contains cellulose, hemicellulose and small percentage of lignin, which generates a small amount of residual ash after combustion. Due to the degradation of the hard materials, it has few nutrients and is used as fertilizer in the field. Significant changes have been observed in the growth of different crops when wheat straw ash is used as fertilizer and the crops are grown under the same climate and cultivation condition in different countries. The ratio of the amount of nitrogen N, phosphorus P and potassium K, are 10–10-10%, respectively in the available commercial fertilizers. The amounts of N, P, and K content in biofertilizers are not similar to those in standard fertilizers. The amount of N, P, and K is nearly 0.45, 0.81 and 2.93 g kg⁻¹ in biofertilizers. Rice-husk ash, CC, and PSA contain a small amount of calcium, potassium, magnesium, etc., and eggshell powder also contains calcium, which could be an alternative source of the minerals in biofertilizers. Omatola and Onojah concluded that agricultural wastes such as rice husk can be used as chemical fertilizers, insecticides, pesticides, and so forth.

### Pyrolysis of rice husk

Rice husks can become a source of energy and have the potential to meet the energy demands of a nation. They have contain large quantities of organic components, so they can act as a potential source of renewable energy. Thermo-chemical processes like pyrolysis are being used to obtain fuels from biomass. Pyrolysis involves the thermal decomposition of organic components present in the biomass waste in the absence of oxygen at ambient temperatures, leading to the production of pyrolysis oil, char, and gaseous fractions. There are two pyrolysis technologies for the conversion, namely slow and fast pyrolysis. Slow pyrolysis involves long reaction times and is mainly used for producing biochar. Fast pyrolysis is currently a very widely used pyrolysis system. Fast pyrolysis is performed in the absence of oxygen at a temperature range of 450 to 600 °C under atmospheric pressure. A short vapor residence time (< 2 s) along with high biomass heating rates produces high liquid output. Despite the advances made in past years, pyrolysis still faces certain challenges like enhancing the yield and quality of biofuels and improving the energy efficiency of the whole process. Microwave-assisted pyrolysis is considered a promising technique. The conventional method of heating is considered slow and inefficient as it transfers heat from the surface to center of the material. In contrast, microwave irradiation results in rapid, efficient in-core volumetric heating. This process enhances the fast pyrolysis and is expected to enhance bio-oil production.

Tsai et al. conducted fast pyrolysis of RH in a fix-bed induction heating system. They studied the effect of fast pyrolysis temperature, heating rate, holding time, gas flow rate, condensation temperature, and particle size on the product yield. The highest oil yield of 40% was obtained under the optimum conditions. Heo et al. studied the optimal reaction conditions for producing bio-oil using fluidized bed reactor and obtained the highest bio-oil yield of approximately 60%. It has also been found that a conical-spouted bed reactor (CSBR) improves the bio-oil yield from fast pyrolysis of RH due to high heat and mass transfer rates. Alvarez et al. found that the bio-oil yield of 70% could be obtained from fast pyrolysis of RH in a CSBR. Efforts are continuously being made to improve the bio-oil yield, to allow its industrial production. Mostly flash pyrolysis is used to obtain a high yield of bio-oil with different useful bio-products like char (solid residue). It can also be used for getting activated carbon and amorphous silica. Table 4 gives a comparison of the bio-oil yield output obtained from different reactors and their optimum conditions.
Different treatments, like sodium hydroxide and potassium hydroxide activation, have been used to improve the activated carbon content output.\(^\text{140-142}\) There have also been studies to understand the influence of potassium and zinc chloride on the synthesis of activated carbon.\(^\text{143,144}\) Table 5 shows the value of the surface area of activated carbon obtained from pyrolysis of RH by different chemical activation methods.

It has been reported that activated carbon obtained from RH be used in water and air purification. Moreover, it could be used as anode material for lithium-ion batteries and for supercapacitors.\(^\text{145-148}\) Rice-husk pyrolysis has also been used to generate syngas, which can be used to produce electricity.\(^\text{149,150}\)

Various pre-treatments have been employed to enhance the quality and quantity of yield obtained from pyrolysis of biomass. Torrefaction is one such method, which involves a pre-treatment at 200–300 °C under an inert atmosphere and at a low heating rate. Torrefaction results in improved quality of fuel because of the removal of around 9.5–63.2% oxygen at a temperature range of 210–300°C. It has been found that, on increasing the torrefaction temperature, improved gaseous and liquid energy yields can be obtained.\(^\text{151}\) Chen et al.\(^\text{152}\) studied the effects of torrefaction on the pyrolysis of RH and concluded that this process improves the content of many high-value products, mainly laevoglucose. Zhang et al.\(^\text{153}\) also concluded that torrefaction and water washing of RH increase the levoglucosan content by nine times, as shown in Table 6.

Zhang et al.\(^\text{155}\) studied the combined effects of water washing and torrefaction on the pyrolysis of RH during microwave heating. It was found that this pre-treatment removed a large amount of inorganic waste, enhanced fuel characteristics and the quality of gas. Zhang et al.\(^\text{154}\) also used wet torrefaction to improve the yield of bio-oil from pyrolysis of RH. It was concluded that the amount of levoglucosan was around 6.2% higher than that obtained from raw RH, and this pre-treatment can enhance the quality of bio-oil. Zhang et al.\(^\text{156}\) also investigated the influence of torrefaction on the char yield. It was suggested that torrefaction increases char and also improves the yield and quality of activated carbon.

The literature has shown that the use of catalysts during pyrolysis can enhance the yield and lower the energy input. Williams and Nugranad\(^\text{157}\) used zeolitescony mobil-5 (ZSM-5) as the catalyst for RH pyrolysis in a fluidized bed reactor. It was found that at a lower catalyst temperature the oxygen in the pyrolysis oil was converted by the catalyst primarily to H\(_2\)O and at higher catalyst temperatures largely to CO and CO\(_2\). Abu Bakar and Titiloye\(^\text{158}\) used ZSM-5, Al-MCM-41 and Al-MSU-F as catalysts for the catalytic pyrolysis of Brunei RH. They compared the bio-oil yield of these catalysts, as shown in Table 7. Zhou et al.\(^\text{159}\) studied the influence of a mild catalyst, zinc oxide, on the bio-oil yield of RHA pyrolysis and obtained a maximum yield of 49.91% at 550 °C. Zhang et al.\(^\text{160}\) attempted to achieve the highest
possible gas yield from the microwave pyrolysis of RH using Ni, Fe, and Cu as catalysts. It was found that a Ni catalyst produces the highest gas yield. Loy et al. presented a novel idea of using industrial waste coal bottom ash as catalysts in the pyrolysis of RH. A comparison was also made between the commercial catalysts (natural zeolites and nickel) and coal bottom ash. Fu et al. used KOH as catalyst for the pyrolysis of RH and produced activated micro-mesoporous bio-carbon with a high specific area.

### Agro-waste for heat generation in mills and power plants

It has become necessary to search for clean energy sources to reduce greenhouse gas emissions. Due to a global decline in fossil fuel reserves in recent decades, there is a growing need for clean energy across the world to meet ever growing energy demands. The primary sources of electricity production are hydro, thermal, and nuclear plants, with a capacity of 6858, 15 440, and 750 MW, respectively. Inadequate energy supplies, power shortages, and load shedding have been posing a challenge in developing countries due to increasing population and energy demands. Agro wastes like RH are being used as fuel in the boilers to generate steam for generator turbines to provide electricity. However, this produces very high amounts of silica, which may limit its application. Moreover, it has been reported that biomass could be used for the production of ethanol and hydrogen. Combustion, gasification, and pyrolysis are being used to generate the fuel.

### Second generation agricultural wastes and their uses

Agricultural wastes are used to generate heat in mills and power plants, which produce ashes as secondary products. Ashes of agro-food waste create environmental and health issues due to the fumes and the small particle sizes that they produce. Finding ways to use them to make value-added products is essential. These ashes and some selected food wastes are used to develop value-added engineering and medical materials. In general, agro-waste ashes contain 22% carbon-content, with variable 30–78% SiO$_2$ along with K$_2$O, Na$_2$O, MgO, P$_2$O$_5$, and some other trace elements. The oxide content depends on the atmosphere, quality of soil, and the use of pesticides. The chemical composition of various agro-waste ashes along with food wastes are shown in Table 8. As observed from the Table 8, the most common inorganic component is SiO$_2$, apart from alkali and alkaline-earth metal oxides.

Different techniques like sol gel, co-precipitation, and simple acid and alkali treatments are being used to extract various amounts of silica from RH wastes, as shown in Fig. 3. Apart from the extraction of silica from agro-food wastes, there are many other possible applications in various engineering fields covered in the following sections. Based on the presence of different metal oxides, these ashes can be used in cement and construction materials, glasses and glass-ceramics, or silicate-based ceramics, as discussed below.

### Use in construction materials

The cement and construction industries are utilizing agro-waste ashes to enhance the properties of cement. Many researchers have found that by adding RHA, SCLA, WSA, and some other residue ashes of the wastes to cement, it is possible to improve the durability and mechanical properties of the cement. Sandhu and Siddique concluded that RHA acts as a concrete filler with reduced land-filling costs and also provides a cleaner sustainable environmental solution, saving energy and reducing carbon dioxide generation by cement consumption. The ground ash of RH is partially filled in cement concrete, which improves the properties of the concrete. The addition of the 10 wt% RHA in composite can improve the compressive strength, fire, and acid resistance of the as-prepared composite, which is suitable for making load-bearing bricks for buildings. Nair et al. examined mechanical properties like compressive strength and flexural strength of ordinary Portland cement (OPC) when replaced with rice husk ash up to 25 wt%. The compressive strength increases for water/binder ratios: 0.35 and 0.4, beyond 0.45, the compressive strength of OPC decreases. The maximum compressive strength is obtained for 0.4 water/binder ratio for 25 wt% replacement of RHA with OPC for concrete cubes. Due to pozzolanic properties and the filling ability of RHA, the compressive strength of concrete cylinder containing 25 wt% RHA is more than that of ordinary concrete. Up
to 30 wt% RHA enhanced the mechanical strength and durability of cement.\textsuperscript{177} The incorporation of 10–15 wt% RHA as a partial replacement for cement enhances the strength and durability properties of self-compacting cement (SCC). Ali \textit{et al.}\textsuperscript{178} reported that 10–50 wt% of RHA added with alumina creates more porosity and new phases like cristobalite and corundum (an Al$_2$O$_3$-related phase), which increase the tensile strength and compressive strength of the concrete. Mehta\textsuperscript{179} has found that when RHA is replaced with cement up to 50 wt%, higher compressive strength than that of ordinary Portland cement concrete can be achieved. Zhang \textit{et al.}\textsuperscript{180} investigated the influence of 10% RHA inclusion as a partial replacement of OPC on the compressive strength of concrete and compared it with the compressive strength of concrete containing 10% silica fume (SF). At 28 days curing the RHA concrete had a compressive strength of 38.6 MPa compared with 36.4 MPa for the control concrete (100% OPC) and 44.4 MPa for SF

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline
\textbf{Compounds} & \textbf{RHA (wt\%)} & \textbf{SCBA (wt\%)} & \textbf{CHA (wt\%)} & \textbf{PSA (wt\%)} & \textbf{WSA (wt\%)} & \textbf{Barley ash (wt\%)} & \textbf{CCA (wt\%)} & \textbf{ESP (wt\%)} & \textbf{Banana peel (wt\%)} \\
\hline
SiO$_2$ & 91.03 & 65.8 & 35.7 & 29.3 & 73.95 & 62.04 & 25.68 & 0.10 & 6.6 \\
CaO & 1.95 & 4.2 & 5.80 & 21.9 & 5.21 & 4.48 & 4.08 & 98.6 & 3.2 \\
MgO & 0.81 & 1.7 & 9.91 & 6.7 & 1.83 & 2.16 & 5.38 & 0.24 & 1.3 \\
K$_2$O & 3.18 & 7.5 & 20.1 & 25.7 & 11.51 & 19.27 & 31.23 & 0.10 & 67.6 \\
Na$_2$O & 0.08 & 0.6 & 5.10 & 0.1 & 0.44 & 8.40 & 0.10 & 3.2 \\
Al$_2$O$_3$ & 0.35 & 5.5 & 0.40 & 3.7 & 0.91 & 0.19 & 1.74 & 0.3 \\
Fe$_2$O$_3$ & 0.33 & 0.30 & 1.0 & 1.51 & 0.17 & 2.65 & 0.2 \\
P$_2$O$_5$ & 0.25 & 22.5 & 0.3 & 2.52 & 0.2 \\
SO$_3$ & 0.2 & 3.2 & 1.42 & 0.71 & 0.3 \\
TiO$_2$ & 0.05 & 0.44 & 0.02 & 0.3 \\
MnO & 0.05 & 0.10 & 0.61 & 0.1 \\
Cl & — & — & — & — & — \\
\hline
\end{tabular}
\caption{The various wastes ashes in oxides and their weight percentage in rice husk ash (RHA), sugarcane leave ash (SCLA), corn husk ash (CHA), peanut shell ash (PSA), wheat straw ash (WSA), barley ash, coconut ash (CCA), eggshell powder (ESP) and banana peel.\textsuperscript{10,72,168,169}}
\end{table}
concrete. Waswa-Sabuni et al.\textsuperscript{181} examined the engineering properties of binder resulting from a mixture of OPC with RHA. They established that the compressive strength of OPC/RHA concrete cubes increased with increasing RHA. Abdelalim et al.\textsuperscript{182} studied the effects of using RHA as a cement replacement material on the compressive strength of cementitious materials in a controlled experimental program. It was found that the incorporation of RHA in OPC mixes led to a notable increase in the compressive strength. Ajiwe et al.\textsuperscript{183} successfully produced white Portland cement using RHA as a raw material. It was of the same standard as commercial white Portland cement: 24.5\% RHA was mixed with other raw materials (sourced locally) to produce white Portland cement and the cement that was produced was used to make a concrete slab. Javed et al.\textsuperscript{184} has investigated the use of fiber waste, RHA, and limestone powder waste as cement replacement materials for lightweight concrete blocks. The water absorption and bulk density of concrete can be reduced by adding RHA. The test results showed that lightweight concrete could be produced by adding RHA. Shatat et al.\textsuperscript{185} investigated the chloride and chemical resistance of SCC containing RHA and Metakaolin (MK). A good synergistic effect between MK and RHA on the mechanical properties and durability of SCC were observed. Cisse and Laquerbe\textsuperscript{186} reported that, after the addition of RHA into cement the physico-mechanical performance of the final products can be improved. Cement with RHA added has a lower cost than cement with other types of additions.

Jauberthie et al.\textsuperscript{187} also reported that the polozon of the agro-wastes could be used for making lower cost cement and this silica can be reused in many other applications. Nambirajan\textsuperscript{188} investigated the use of RHA to reduce the temperature in high strength mass concrete and found that RHA is very effective in reducing the temperature of mass concrete compared to OPC concrete. Banger et al.\textsuperscript{189} suggested that the strength of the concrete can be improved after adding sugarcane bagasse ash (SCBA) up to 10 wt\%.

Dhengare et al.\textsuperscript{190} studied the effects of use of SCBA on the mechanical strength of concrete by partial replacement of cement at the ratio of 0, 10, 15, and 20\%, by weight for compressive strength. Alavéz-Ramírez et al.\textsuperscript{191} concluded that the addition of 10\% of SCBA in combination with 10\% of lime significantly improves the mechanical and durability properties of compacted soil blocks. At the same time, the addition of a certain amount of SCBA improves the flexural compressive strength of water-saturated compacted blocks prepared with only soil and lime. This combination of SCBA and lime as a replacement for cement in the stabilization of compacted soil blocks seems to be a promising alternative when considering issues of energy consumption and pollution. Singh et al.\textsuperscript{171} reported that the 10 wt\% calcined SCLA at 600 °C, replaced with OPC can enhance the compressive strength comparable to that of OPC at 28 days of hydration.

Shu-Ing and Choo\textsuperscript{192} reported that the ESP added up to 0–15 wt\% increases the compressive strength and flexural strength, which also decreases the water absorption power. Cobreros et al.\textsuperscript{193} reported that, by mixing barley ash in certain amounts in cement, compressive strength can be improved. Pappu et al.\textsuperscript{3} reviewed that the agricultural wastes of vegetables, food products, tea, oil production, jute fiber, groundnut shell, wooden mill waste, CH, cotton stalks, etc., could be used in cement and construction materials. Kreiker et al.\textsuperscript{194} suggested that the use of peanut shell ash (PSA) up to 15 wt\% is very beneficial for increasing the compressive strength without altering the mechanical properties of the cement. This waste ash could be used for pollution reduction in the cement industry. Raheem et al.\textsuperscript{195} have reported that groundnut shell ash (GSA) could be used for light load-bearing elements. Alabadan et al.\textsuperscript{196} investigated the potential of GSA as a partial replacement for ordinary Portland cement in concrete. In this study, it was reported that the strength of the mixture was higher and concluded that the replacement of cement with up to 30\% ash gave promising results. Mahmoud et al.\textsuperscript{197} studied the effect on the mechanical properties of cement of replacing up to 50 wt\% with GSA. GSA (K$_2$O rich) could be used as filler in cement, as it enhances the mechanical properties such compressive strength. Overall, agro-food wastes ashes can be used in cement, bricks, and other construction materials. This approach not only decreases the cost of conventional construction materials but also increases the mechanical properties of the product.

**Glasses and glass ceramics derived from agro-waste ashes and ES wastes**

Glasses and glass ceramics are being used in the field of engineering and medical science, for example as sealing materials in solid oxide fuel cells, non-linear optics, lasers, substrates in solar energy production, treatment of cancer, etc.\textsuperscript{198–207} These glasses and glass ceramics are synthesized using different mineral oxides, which are costly.\textsuperscript{208,209} Recently, some reports have appeared in the literature according to which properly selected agro-food waste ashes could produce these glasses, ceramics, and glass ceramics. The selection of different agro-food waste ashes depends on the product’s intended application. In the following sections, the synthesis of glasses, ceramics, and glass ceramics synthesized from agro-food waste ashes is discussed.
Their applications, particularly in the field of optics, dielectrics, and biomaterials, have been summarized.

Optical materials

Agro-food wastes ashes could be used to synthesize glasses and glass ceramics for optical devices, windows, and some other applications. For instance, fused silica glass can be made at very high melting temperatures using RHA as a resource because the silica content in RHA is ~90–95 wt%. The addition of ESP in RHA is also known to decrease the melting point of glasses because CaO (ESP) acts as a modifier and can modify the properties of the glasses. Cornejo et al. reported that a typical window glass (soda lime) could be synthesized from RH and ES with a small amount of table salt and alumina. It is also known that the silicate matrix acts as a suitable host for producing phosphors. Lakshmi Devi and Jayasankar used ES and RH to synthesize monoclinic Ca$_2$SiO$_4$ doped with Dy$^{3+}$ and Eu$^{3+}$. The photoluminescence data showed white and red light emissions, respectively; hence they can be used in the production of LEDs. Sharma et al. synthesized glasses and glass ceramics using rice husks and sugarcane ashes. The photoluminescence data indicated that these can be used in ultra-violet blue LEDs. The same group has also synthesized glasses using ES along with CHA and SCLA and observed photoluminescence in the UV-visible region. Punj and Singh used CHA, SCLA, and ESP to synthesize silica phosphate glasses. Due to the presence of inherent trace elements, these glasses emit blue-green light. Kaewkhao and Limsuwan used RH to produce glasses doped with Cu, Mn, Zn, Er, and Co, and concluded that RH can be used for colored and colorless glass production. Erbium is an important glass dopant and finds application in communication technology for optical signal amplification. Umar et al. synthesized erbium-doped RH silicate borotellurite glasses and studied their optical, structural and physical properties. Lee et al. used RH to produce a glass, to which green photoluminescent (PL) pigment was added. The pigment was added using two different techniques, namely layering and mixing methods. In the layering method, the PL was pigmented and was added in the center of casted glass forming a sandwich-like structure. In the mixing method, the PL pigment was directly added into the molten glass. It was found that the layering technique resulted in lower decomposition of PL pigment as this method exposed lesser PL pigment to high temperature; hence, resulted in better PL properties. Apart from these, researchers have studied the effects of MnO$_2$ and ZnO concentration on the optical properties of zinc silicate and borotellurite glasses derived from RHA.

It is a matter of common knowledge that gamma rays are harmful; hence, a number of glasses have been synthesized for the purpose of radiation shielding. Such glasses are important because they are transparent to visible radiation and hinder gamma rays. Glasses containing Bi$_2$O$_3$, BaO, and PbO have shown good radiation-shielding capability because of their high mass attenuation coefficient and low value of half-value layer parameter. Tuscharoen et al. studied the structural, optical, and radiation-shielding properties of barium-borate-RHA glasses. It was suggested that such systems could have potential applications in gamma-ray shielding. Ruengsri et al. used RHA to produce barium borosilicate glasses and studied their radiation-shielding capabilities. It was found that these glasses possessed good optical transparency and could be used as radiation shielding materials. Mustafa et al. fabricated glasses with the following composition: xBi$_2$O$_3$-(1-x) ZnO-0.2Bi$_2$O$_3$-0.3(SiO$_2$), and studied their potential for radiation shielding. It was found that the mass attenuation coefficient increased with the increase in the Bi$_2$O$_3$ content and could act as good transparent radiation shielding material. Recently, Sudiana et al. used RHA to synthesize silica xerogels, which were mixed with SnO$_2$. It was found from the microstructural and optical properties of the material that these could be a potential candidate for ceramic waveguide materials.

Dielectric materials

Dielectric permittivity, dielectric loss factor, and conductivity with different rice bran (RB) content have been measured. It was found that dielectric permittivity, dielectric loss factor, and conductivity decreases with an increase in RB content. Such behavior may be attributed to the reduced number of mobile carriers. The inherent porosity of the glasses and glass ceramics synthesized from the ashes of agro-food waste decreases the thermal conductivity, dielectric permittivity, and density of the glasses compared to conventionally synthesized glasses. On the other hand, it enhances the sensing and absorption of sound waves. So, these glasses and glass-ceramics can readily find applications in the microelectronic devices, such as band-pass filters, dielectric resonant antennas, and oscillators. For these applications, the material should have dielectric permittivity ~10 or above at room temperature with good thermal and mechanical stability. It also must have temperature and frequency independent behavior in the microwave frequency region. The dielectric and optical properties of the RHA and SCLA based samples were reported by Danewalia et al. They observed dielectric constant~7–25 with discrete temperature up to 600°C and conductivity was small for these samples. Inegbenebor and Adeniji investigated the dielectric insulation properties
of seven selected agro-waste materials (shells of coconut, mango, palm kernel, beans and groundnut, and corncob and rice husk) bound with gum arabic. The values of dielectric constant are ~3.5-5.5 for the materials derived using coconut shell, palm kernel and PSA. These waste materials could be used in high-voltage applications. Mango shell, corncob, RH, and bean shell derived materials posses low dielectric constants (less than 3.0), hence can find use in low voltage applications. On the other hand, RHA microwave absorbers have been synthesized and reported by Liu et al. Very low value of bulk density has been reported for these materials, i.e., 0.4 g cm$^{-2}$. With advantages such as high electromagnetic (EM) wave absorption, low density, low cost, and environmental friendliness, RHA is a promising lightweight EM wave absorber.

### Biomaterials

Eggshell membrane is a low porosity semi-permeable membrane consisting of fibrous protein (collagen). Eggshell membrane is bioactive and biocompatible due to the natural presence of biomaterials such as collagens type I, V and X. These have potential clinical, cosmetic, nutraceutical, and nanotechnology applications. Eggshell membrane contains glycosaminoglycans such as dermatan sulfate and chondroitin sulfate, sulfated glycoproteins including hexosamines, and hyaluronic acid, hence it is used for the treatment of osteoarthritis. Brunello and Masini reported that natural ESM can be utilized for the treatment of osteoarthritis. It can reduce knee pain and increase flexibility in joint and connective tissue disorder due to the presence of naturally occurring glycosaminoglycans and protein. Various studies also reported that ESM has a useful effect on cutaneous wounds in the early stages of healing. Yang et al. found that the ESM used as a biological dressing for burn wounds acts just the same as a human amniotic membrane. Eggshell membrane also helps in pain relief over the split-thickness skin graft donor site. It could be used in healing acute traumatic tympanic membrane and traumatic lip laceration.

Various studies also reported that infection inhibits wound healing. Liu et al. introduced an optimal quantity of Ag nanoparticles into microfibers of the natural eggshell membrane (NEM) as mussel-inspired dopamine (DA). This prevents bacterial infections in wounds by damaging the bacterial membrane and DNA. These nanoparticles not only enhanced wound dressing for cutaneous wounds but also exhibited good biocompatibility and anti-inflammatory properties. Some studies have reported that scaffolds can be used to release proper doses of drugs that depend on cytotoxicity of silver nanoparticles (AgNPs).

Vuong et al. reported that processed ESM powder and its soluble carbohydrate components exhibit anti-inflammatory and immune modulator properties in monocytes and macrophages. Eggshell membrane was also used for soluble eggshell protein (SEP) immobilization by electro-spinning method for tissue engineering applications. Polycaprolactone (PCL) has good mechanical strength and, in combination with weak SEP, has a great potential as scaffold material and guided tissue regeneration barrier material. Processed eggshell membrane (PEP) also acts as skin wound healing activator. Processed eggshell membranes with its fibrous structure and collagen components enhances fibroblasts and keratinocytes, which migrate into the wound and start to proliferate. This regulates the activity of various increased matrix metalloproteinase type 2 enzymes that affect early cellular events during wound healing. Eggshell membrane has found uses in eye engineering as a dressing model that was developed for the use of vitreous surgery training as well as in nerve regeneration. Hence, ESM is a promising biomaterial for the preparation of wound dressings and nerve regeneration.

Different bioglasses and bio-ceramics are being developed, focusing on a variety of biomedical applications (Fig. 4). Bioglass is used in different applications such as orthopedics and dentistry. Attempts are currently being made to replicate its composition using agro-food waste ashes.

Rice-husk ash has been used to prepare amorphous silica for bioactive applications. Three types of amorphous silica, namely brown ash (BA), white ash (WA), and silica gel (SG) have been prepared from rice husk. Brown ash can be prepared by burning husk at 700 °C and it contains about 96% silica. White ash contains 99.78% silica, and can be prepared by combustion and further acid treatments. Silica gel can be prepared from BA through the alkaline extraction of silica and acid neutralization process. The bioactivity of these different ashes evaluated at different temperatures – i.e., 900 °C for BA, 1100 °C for SG and 1200 °C for WA – after dipping into simulated body fluid (SBF) and Tris buffer solution has been reported. Brown ash and SG ceramics show more bioactivity than WA ceramics. This is due to the formation of silanol groups on the surface of the silica particles in the presence of the hydrolysis process. In the case of SG, hydrolysis might be more straightforward due to the inherent gel formation of materials. White ash shows low response for bioactivity due to the presence of fewer impurities when treated at high temperature (1200 °C). The effect of sintering temperature on the mechanical and physical properties of bioactive glasses prepared from agro-food wastes is presented in Table 9.
Textural properties in biomaterials also play an important role in the fabrication of the apatite layer. Increasing the specific surface area and pore volume of bioactive glasses may greatly accelerate the apatite layer formation and therefore enhance bioactive behavior.\textsuperscript{255} Naghizadeh \textit{et al.}\textsuperscript{254} studied different concentrations of silicate-based bioactive glass-ceramic (R-SBgC) with the composition of (mol\%) 50SiO\textsubscript{2}-25Na\textsubscript{2}O-25CaO prepared from RHA combined with PCL to fabricate a composite scaffold using a thermally induced phase-separation method. The results indicate that the increase in R-SBgC/PCL concentration from 0 to 30\% (w/w), produces bioactive material that has an average pore size (105 to 98 \(\mu\)m), increased density (0.062 ± 0.01 to 0.163 ± 0.06), and compressive modulus (0.375 ± 0.02 Mpa to 0.475 ± 0.04 MPa). This resulted in reduced scaffold porosity (80 ± 0.03\% to 76 ± 0.04\%), which has been useful in the development of an ideal scaffold, used as a bone substitute in non-load-bearing sites in the human body. The same research group also reported good bioactivity and biocompatibility on the surface of the R-SBgC prepared by a sol-gel method. Varying the R-SBgC concentrations can also improve mechanical and textural properties such as porosity, density, and pore sizes.\textsuperscript{256} Özarslan and Yücel\textsuperscript{257} also studied bioactive glass scaffolds produced by the polymer foam replica method. The results showed that undoped and Sr-doped RHA silica-based bioactive glass scaffolds had better bioactivity, pore 

\begin{table}[h]
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\begin{tabular}{|l|l|l|l|l|l|}
\hline
Composition & Sintering temperature & Method & Phases & Density (g/cc) & Conclusion & Refs. \\
\hline
SiO\textsubscript{2}-Na\textsubscript{2}O-CaO & >700 °C & Sol-gel & Three phases Combetite-I, \(Na_6Ca_3Si_6O_{18}\) and \(Na_2Ca_2Si_2O_7\) & 2.20 & Good bioactivity, biodegradability & 253,254 \\
&& At 900 to 1000 °C & Sol--gel & Combetite-I, small amount of combetite-II, \(Na_4Ca_3Si_6O_{18}\) & & \\
& >1050 °C & Sol--gel & & & & \\
\hline
SiO\textsubscript{2}-Na\textsubscript{2}O-CaO-P\textsubscript{2}O\textsubscript{5} & 650 to 700 °C & Melt-quench & Hexagonal \(Na_2Ca_3Si_3O_9\) & 2.27 & Good bioactivity & 254 \\
&& At 1050 °C & Melt -quench & \(Ca_3Si_2O_7\) & without affecting of the crystalline phases & \\
\hline
\end{tabular}
\caption{Bioactive properties of silica-based glasses and glass-ceramics derived from rice husk ash at different sintering temperature.}
\end{table}
size, porosity, and high potential to form new bone for bone defects in tissue engineering than commercial silica-based bioactive glass scaffolds. Andreola et al.258 have used RHA for synthesizing SiO₂-Al₂O₃-MgO glass-ceramics by a solid-state reaction technique. The sintered materials have similar bending strength but higher Mohs hardness compared with the commercially available glasses. Shamsudin et al.259 produced β wollastonite using RHA and calcined limestone using an autoclaving method. β-Wollastonite material possesses a porous structure, good bioactivity, and biocompatibility with the cells. This also showed significant degradation as a function of soaking time in the SBF solution. An amorphous calcium phosphate layer was formed when calcium and phosphate ions increased on the wollastonite surface. Such materials offer potential in drug delivery systems.

Recently, mesoporous silica has been prepared using RH (rMBG) through sol-gel processed for anticancer drug delivery and bone regeneration. The grafted folic acid (FA) combined with rMBG can increase the cytotoxicity of camptothecin (CPT), a water-insoluble anticancer drug, toward the cancer cells. This showed a well ordered hexagonal mesoscopic structure, high surface area, and a high pore volume, which has the capability of producing an HA layer that can be connected to the bone. Furthermore, both rMBG and rMBG-FA have no cytotoxicity in normal cells and showed excellent biocompatibility. Rajanna et al.260 reported that high loading and fast-release kinetics of ibuprofen and eugenol which confirmed silica aerogel microparticles (SAMs) is suitable for drug delivery. Later robust silica aerogel microspheres (RSAMs) have been prepared using sol-gel / mineral-oil emulsion method to enhance the fast dissolution rate and bioavailability of poorly water-soluble drugs. Robust silica aerogel microspheres are spherical and less porous structures as compared with SAMs; however, they are stronger and robust and more free-flowing than SAMs. It has been found that RSAMs have a mesoporous structure with a surface area 274 m² g⁻¹, total pore volume 0.67 cm³ g⁻¹, and an average pore diameter of 8.6 nm. This surface area is about 60% less, and the pore volume is 80% less, than that of SAMs.260 Industrial wastes from burnt RH could also become a cheap source of mesoporous silica for applications in the pharmaceutical industry. Porous silica nanoparticles with a diameter of ~70–75 nm was synthesized using ball-milling method. Diameter size depends upon the rotational speed and milling times.

This showed that a nanoporous silica carrier delayed the release of penicillin G. This can be beneficial for the controlled release of drugs.261 Amorphous silica-based porous bioactive ceramics were prepared successfully by a gel-casting method using silica xerogels powder derived from RHA. They showed good bioactivity and ~25% porosity, with 27.5 ± 0.2 MPa mechanical strength.251

Eggshell waste has been used to synthesize nanocrystalline HA by microwave, wet chemical, hydrothermal, and mechanochemical processing methods. Different processing methods influence HA parameters such as particle size, crystalline size, surface area, pH factor, morphology, and physical and mechanical properties, as shown in Table 10. All these parameters directly influence the bioactivity of the material. Hydroxyapatite derived from natural materials such as bovine bone, fish bone, or coral has the advantage

| Table 10. Particle size, crystallite size, surface area, morphology and physical parameters of HA derived using different processing techniques. |
|---------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| **Methods**                      | **Microwave processing method** | **Precipitation or wet chemical** | **Hydrothermal method** | **Mechano chemical method** |
| **Particle size**                | 33–50 nm in length, 8–14 nm in width, 38.91 nm in length, 16.4 nm in width | — | — | 250-255 nm |
| **Crystalline size**             | 21 nm | 33.1 nm | 34 nm | 8–47 nm |
|                                 |                                  | 39.7 nm | 88 nm | |
|                                 |                                  | 44.9 nm | | |
| **Surface area (BET)** (m² g⁻¹) | 106 | — | — | — |
| **hardness (GPa)**              | 4.364 | 4.96 | 5.3–5.12 | |
| **density (g/cc)**              | 3.12 | 3.03 | — | — |
| **Morphology**                  | Spherulite, flower like morphology Needle like shape at 700 microwave power for 15 m irradiation | Agglomeration of irregular shapes with pores Needle or rod form | Fiber like morphology Irregular morphology | Spherical and free from agglomeration |
| **Ca/P ratio**                  | 1.67 | 1.67 | 1.67 | 1.67 |
Recently, Salah Fluorine can replace the hydroxyl.

Some studies also confirmed that ECPC consists of Nano-ESP has recently been used to enhance heat generation in small-scale industries, compost fertilizers, and mechanical methods can reduce management and converting into different value-added materials. Second-generation by-products of agro-food waste ashes could also be used in various medical, civil, and engineering applications. However, extensive research is required for the large-scale use of these renewable and sustainable resources. So, based on the application, these can be selected, extracted and converted into various value-added materials, which can find applications in the medical and engineering fields. Careful selection of wastes and processing techniques can thus result in the generation of multiple value-added materials. The generation of value-added materials using advanced and environmentally viable physical, chemical and mechanical methods can reduce management and environment related problems and also pave the way to new startups and industries.

**Future scope**

Agro-food wastes contain several major and minor organic constituents. Different physical conditions and processing parameters affect the metal and metalloid oxide content present in the agro-food wastes. Using the green chemistry route these constituents can be converted into different value-added materials. Second-generation by-products of agro-food waste ashes could also be used in various medical, civil, and engineering applications. However, extensive research is required for the large-scale use of these renewable and sustainable resources. So, based on the application, these can be selected, extracted and converted into various value-added materials, which can find applications in the medical and engineering fields. Careful selection of wastes and processing techniques can thus result in the generation of multiple value-added materials. The generation of value-added materials using advanced and environmentally viable physical, chemical and mechanical methods can reduce management and environment related problems and also pave the way to new startups and industries.

**Concluding remarks**

A large amount of agro-food waste is being generated due to an increasing demand for food. Agro-food wastes have long been used in various traditional applications like animal feed, heat generation in small-scale industries, compost fertilizers, and different household applications. With advances in processing technology, these wastes are being used to generate value-added materials like bio-oils, activated carbon, fuel gases, and high-grade silica. These applications result in the creation of ashes as a secondary by-product. Agro-food waste ashes (second-generation products) have recently been used to make value-added engineering materials like bioactive glasses and glass ceramics, and dielectric and optical materials. Utilization of these agro-food waste ashes provides a practical and environment friendly way to convert them into value-added materials. These value-added materials could also replace conventionally synthesized mineral-based products. This approach could also provide an effective solution to the agro-food waste management problem.

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