



# Valorization of Rice Husk to Value-Added Chemicals and Functional Materials

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## Abstract

Agricultural waste, such as rice husk (RH), can be utilized directly or by converting it into various value-added chemicals or functional materials. This minireview has two main objectives: the first is to provide collective information about conversion of RH to value-added products via chemical treatments and the second is to enlist with discussion the various functional materials derived from RH. The chemical treatments help remove recalcitrant structure of lignin and allow carbon-rich organic compounds to separate from RH. The useful products obtained from RH through this method are xylooligosaccharides, bioethanol, levulinic acid, butyric acid, vanillin, benzoic acid, etc. The production of functional materials does not require pretreatment of RH. In this method, RH is combined with metals, non-metals, or their oxides to obtain the functional materials. Due to their porous nature, these RH-based functional materials are used in various applications, such as micro- or nano-adsorbents for the removal of harmful organic and inorganic pollutants; as catalysts because of their active catalytic sites; and as electrode materials because of their high surface area and good carbon quality. In this review, the relevant and latest reports about these applications are discussed with critical analysis.

## Graphical Abstract



## Highlights

- Rice husk (RH) is a useful agricultural waste.
- RH can be transformed into useful materials for various applications.
- Value-added chemicals can be obtained on suitable treatment of RH.

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- **RH can be used as a raw material in small industries.**

**Keywords** Agro waste · Rice husk · Chemical treatments · Valorization · Chemicals · Functional materials

## Introduction

Waste management involves a series of processes that are monitored to maintain and regulate proper disposal of wastes, including collection, transportation, and treatment. The purpose of these processes is to make waste harmless to human and environment. A variety of wastes, like agricultural (Duque-Acevedo et al. 2020), biomedical (Ilyas et al. 2020), electronic (Nithya et al. 2021), food (Aldaco et al. 2020), household (Knickmeyer 2020), industrial (Gaur et al. 2020), nuclear (Suh et al. 2020), marine (Balitaan et al. 2020), and gaseous (Bakonyi et al. 2020), need to be disposed or recycled taking into consideration the environmental concerns. If not properly dealt it finally ends up as an unwanted material in a huge landfill and it pollutes the environment; hence, better planning is needed for its disposal (Nehrenheim 2014). Wastes can also be processed into valuable materials in some cases through regulated practice and by having some knowledge about its nature. In particular, the agricultural waste biomass can be used as functional materials or can be converted to a number of valuable products upon various treatments. Some of the unwanted agricultural biomass (agro wastes), such as rice straw, rice husk (RH), sugarcane bagasse, etc., get accumulated after each harvesting season and they need to be disposed properly. They are usually burnt to free the land space for next agricultural cycle and this method of disposal is not environment friendly. But they can be collected, modified, and utilized to produce some valuable materials. RH is the hard covering of silica and lignin which shields the rice during its growth. Burning of RH produces high ash content (92 to 95% silica) which is porous with high surface area (Azadi et al. 2011; Phonphuak et al. 2015). Due to their adsorbing and insulating properties, RH is useful for many industrial applications. The 2019/2020 crop year data showed that 497.7 million metric tons of milled rice was produced all over the world and India stands as the second largest producer of rice (Bhuvaneshwari et al. 2019). Environmental pollution due to mismanagement of waste from rice production is a serious problem, and thus, utilizing it for obtaining useful products instead of disposing or burning will be a good waste managing practice. As RH may induce irritation in the gut of animals due to their high fiber and silica content, it is usually not recommended for cattle feed owing to its low digestibility and low protein content (Vadiveloo et al. 2009). Studies reported that RH can be used for weight gain in birds. However, this cannot be the sole supplement and

additives are required to complete their diet (Rezaei et al. 2014). Hence, utilizing RH as raw material for production of valuable substances does not interfere with feeding habits of animals.

Herein, we have reviewed most of recent reports in the literature about the use of RH as such or transformed into other materials for various interesting applications. We have also reviewed the various chemicals derived from RH. The valorization of any waste material into useful products is very important as it not only solves the waste disposal problem but also can generate some income. A considerable number of reports on the RH or RH-derived materials prove that this agricultural waste can be easily transformed into number of useful products. The collective information provided in this review points out the significance of RH as raw material for the preparation of useful materials applicable in different fields.

## Rice Husk (RH)

RH contains 25–35% of cellulose, 18–21% of hemicellulose, 26–31% of lignin, and 15–25% of silica (Beaino et al. 2022). RH is used as it is, for example, as an organic fertilizer (Geethakarathi 2021). RH does not affect plant growth regulation in direct means, but it can be used as a medium for gardening because it allows drainage and retains less water. It is also used in some pillow stuffing, brewing beer, for making cardboards, cutleries, etc. (Liu et al. 2016). Suhot et al. (2021) reviewed the use of RH to improve properties of polymers which can be thereafter used in photonics, construction materials, automotive, furniture, etc. However, a durability check is required to conclude their exact application (Suhot et al. 2021). Akhter et al. (2021) reviewed RH as a green material for construction and also mentioned RH-derived material as a catalyst in the transesterification of fatty acids to give biodiesel (Akhter et al. 2021). Bisht et al. (2020) reviewed the application of RH as a fiber with various polymers and techniques that can further enhance the mechanical properties of RH. This study throws light on the preparation of RH-based bio-composites and their applications (Bisht et al. 2020). Prasara et al. (2017) reviewed RH as an economical fuel source which is obtained on direct combustion and gasification. It is also a good source for electricity generation (Prasara et al. 2017). Most often RH is burnt to ash and fly ash. Fly ash is the lighter ash content which sticks to the chimney. Amran et al. (2021) reviewed fly ash-based materials from various sources, like coal, agricultural waste, slag, etc., and RH was also focused with respect to the formation of fly ash (Amran et al. 2021). The ash that is of higher weight is widely used in ceramic

industry by extracting silica (Hossain et al. 2018) and producing silica-based materials (Shen 2017).

Goodman et al. (2020) reviewed about the overall composition and conversion of RH and rice straw using different methods to obtain value-added products. These include agricultural amendments (medium for mushroom production, animal husbandry, soil treatments, etc.), energy production (fuel, alcohol etc.), environmental adsorbents, construction materials (additives, abrasive agent etc.), and various speciality products (silica, lactic acid, xylitol, levulinic acid, etc.) (Goodman et al. 2020). The applications of RH in various forms are shown in Fig. 1.

The most widely used products of RH are silica, activated carbon (AC), and rice husk ash (RHA) and to some extent carbonized rice husk (CRH). Silica is an important product of RH as it is used in many industries, like ceramic industry, cosmetics, as an anticaking agent in food industries, for vulcanizing rubber, as thermal insulators, as fillers for composite, paint industries, electronics, etc. When silica is prepared at high temperatures above 1100 °C, crystalline silica (Nabil et al. 2018) is obtained and on the other hand amorphous silica (Yalçin et al. 2001) is prepared between 500 and 900 °C. Mesoporous silica which is synthesized using tetraethyl orthosilicate (or its derivatives) is a relatively expensive silica source (Costa et al. 2019). Hence, RH a cheap and abundantly available silica source is utilized by many researchers. RH being cost-effective, easily available, eco-friendly, and rich in silica can also act as bio-adsorbent (Abdel-Khalek et al. 2020).

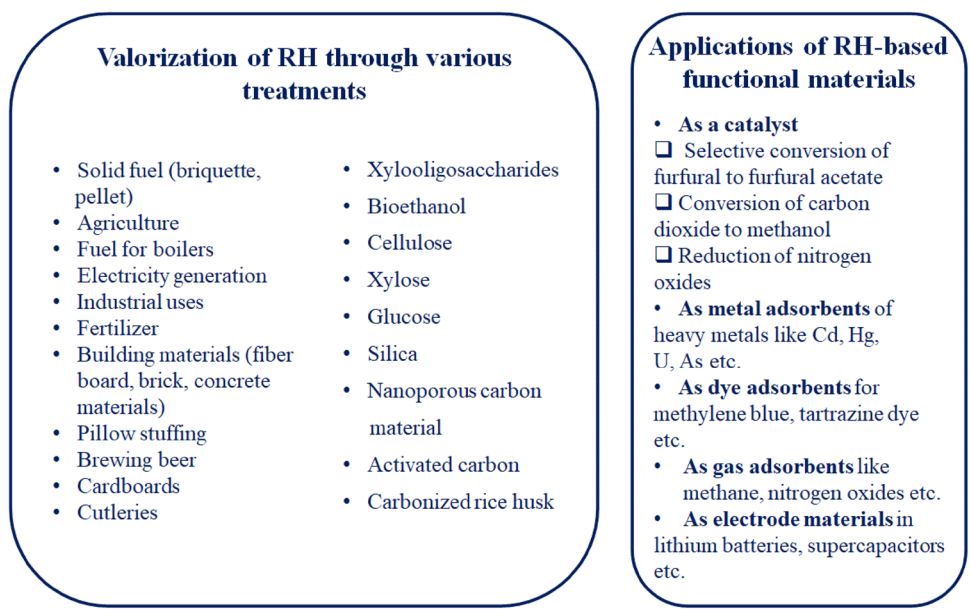
Silica can be prepared to produce nanofluids which finds application in solar thermal installations, automobiles, electronic cooling, biomedicines, etc. (Zhang et al. 2016). The silica content from RH is extracted mainly by alkali

treatment. Along with silica (SiO<sub>2</sub>), silicon (Si), silicon carbide (SiC), and silicon nitride (Si<sub>3</sub>N<sub>4</sub>) are also synthesized using following chemical treatments shown in Scheme 1.

Many studies have also reported AC sorption (El-Bery et al. 2022). These AC can be formed from lignocellulosic materials. Although so many other methods have been developed for the removal of pollutants, adsorption is considered to be one of the profitable as well as flexible methods due to its high efficiency, low cost, low maintenance, and superior regeneration capacity (Demirbas et al. 2008).

A few works have been published that report the burning of RH at high temperature to produce AC, which is an excellent adsorbent and is extensively used in various industries (Cheah et al. 2016; Menya et al. 2018; Alam 2020). AC has a porous structure which makes it suitable for adsorption of metals, organic waste, etc., as well as for catalytic purposes. There are many types of AC which are granular AC, powdered carbon, extruded carbon, etc. Higher the internal surface of the carbon, higher is the effectiveness and mostly has an internal surface area of 500 to 1500 m<sup>2</sup>/g or even more. ACs have wide applications, like waste water treatment, air purification, purifying electroplating solutions, as an ingredient in cosmetics and medicines, in fuel storage, as catalysts, in industries, etc. (Delgado et al. 2015). AC obtained from RH can show possible use in supercapacitors and electrodes for lithium ion batteries (LIBs) (Chen et al. 2021). Thermal decomposition of biomass under a limited supply of oxygen is called carbonization. CRH is obtained by combustion of RH at 700 °C (Ismagilov et al. 2009) and is carried out in the presence of CO<sub>2</sub> or steam, or a mixture of both to remove non-carbon elements, such as nitrogen, oxygen, and hydrogen thereby creating pores. This material when activated using some agents helps in the removal

Fig. 1 Applications of RH in its various forms



**Scheme 1** Conversion of silica to useful silica derivatives (Patil et al. 2017)

### Treatment with alkali (NaOH) to give sodium silicate



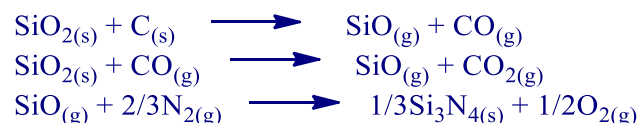
### Obtaining silica from sodium silicate



### Synthesis of silicon carbide



### Synthesis of silicon nitride



### Amorphous silicon from silica

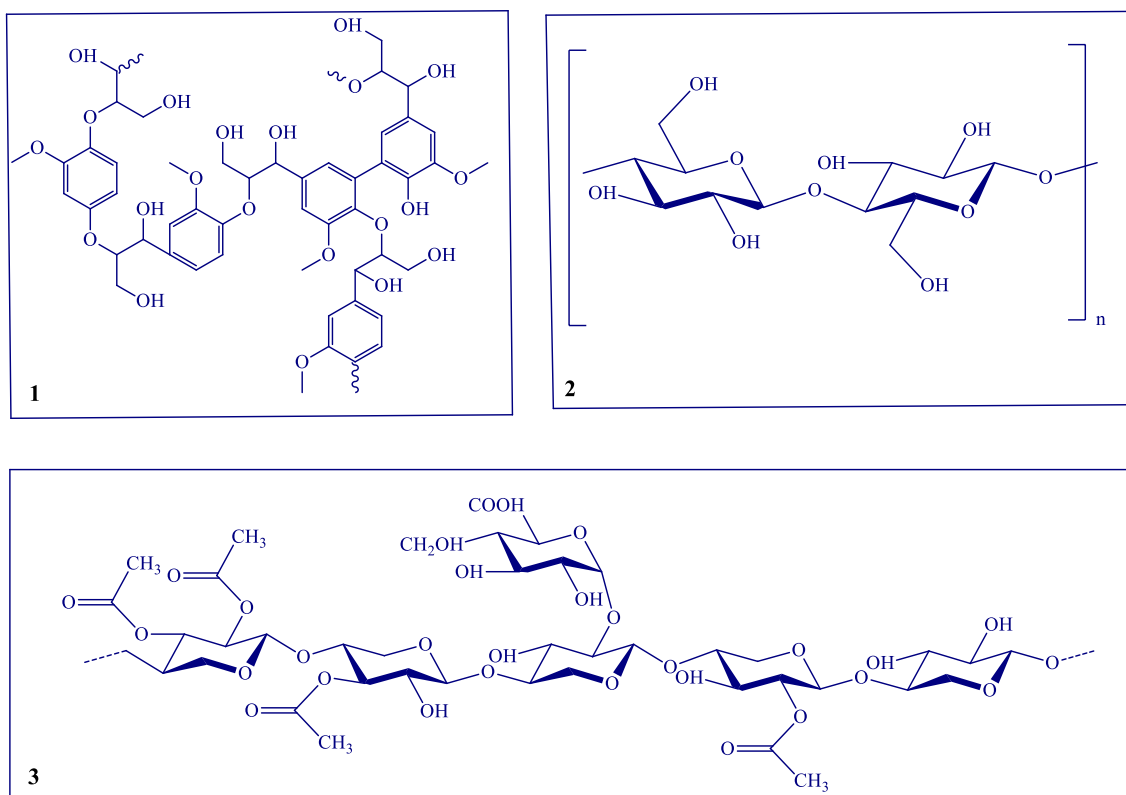


of disordered carbon which might block the pores in CRH (Yang et al. 2010). Due to the high adsorbing capacity of CRH, it is mainly used as soil fertilizer as well as a soil substrate. Studies conducted on characterization of raw rice husk and CRH show that the latter one is around 30% finer. Hydrothermal carbonization is a process of breaking down plant cell wall which leads to rapid conversion of biomass into carbon-rich product (Heidari et al. 2019), such as bio-char (Hossain et al. 2020).

Every 100 kg of RH burnt in a boiler will yield about 25 kg of RHA (Singh 2018). RHA has several applications and there are already a few reviews on the same. The applications include using RHA in refractory industry to produce bricks (Munir et al. 2021) and concrete materials (Siddika et al. 2018, 2021; Elakkiah 2019). Moayedi et al. (2019) reviewed RHA as a compatible concrete material due to its pozzolanic property as it contains 90% silica making it highly amorphous with greater surface area (Moayedi et al. 2019). Fapohunda et al. (2017) reviewed applications of RHA as concrete materials. This study reviewed that RHA is capable of producing more porous and thermally stable bricks as it lowers the compressive strength and density of the specimen. This study mentioned RHA as an alternative source for Portland cement which can help in environmental friendly construction of roads and buildings (Fapohunda et al. 2017). These can serve as alternatives for construction of roads where the traffic load is less or in rural areas

where there is a shortage of cement. The geographical location of crop and the parameters used to prepare RHA is an important aspect to be noted to fix their properties. RHA has proven to be corrosion resistant and hence cracking can be prevented (Saraswathy et al. 2007; Moayedi et al. 2019). The presence of  $\text{SiO}_2$  in RHA can prevent the massive ecological issue of the cement industries since the former can be used as cement or their additives. However, due to different conditions of heating, it is important to check the durability of these cementitious material. The various durability testing parameters are permeability of fluid, shrinkage of the material, thermal conductivity and resistance, fire resistance, effects of high and low temperatures, acid attack, etc.

Apart from the above-mentioned products from RH, several other products are also possible since they are carbon-rich materials. RH also contains lignocellulosic biomass, which resists degradation due to the strong crosslinked structures of three polymers—lignin (1), cellulose (2), and hemicellulose (3) (Fig. 2) via ether and ester linkages in the plant cell wall. Hence, it becomes important to remove the crosslinks before processing of RH to useful chemicals. Pretreatment is one such technique which can help in separating the components (lignin, cellulose and hemicellulose) or by removing lignin and make cellulose and hemicellulose more accessible to enzymes to obtain useful products (Cheng and Stomp 2009).



**Fig. 2** 1: Lignin; 2: cellulose; and 3: hemicellulose

In the next section, the first objective of this minireview, i.e., valorization of RH through chemical treatments, will be focused.

### Conversion of RH into Value-Added Chemicals

There are several types of pretreatments, such as acid, alkaline, hydrothermal, steam, washing at high temperature, ionic liquids (ILs), etc. The chemical treatments are more commonly used than thermal treatments (Shamsollahi et al. 2019). Alkaline pretreatment is required to remove silica from surface of RH as removal of it results in higher porosity of the carbonaceous surface which gives better adsorbing AC (Bakar et al. 2020). Alkaline pretreatments are usually recommended more than acid pretreatments due to their capability of removing more lignin (Baruah et al. 2018). But alkaline pretreatment stands with a disadvantage as it requires a lot of water to bring the final pH to 7. Acid pretreatments do not require a lot of water washings but both acid and alkaline pretreatments cause corruptions in their upscaling. Because of these reasons, alternative methods are preferred. One of the methods is to pretreat RH lignocellulosic biomass with ILs. ILs are salts with usually

low melting points or mostly liquid at room temperature. They are composed of an organic cation and an inorganic or organic anion. Advantages of ILs over other processing reagents are that they are recyclable, non-volatile, and less corrosive (Gholami et al. 2020). ILs are effective in partially dissolving these polymeric lignocellulosic structures because of their ability to breakdown inter- and intramolecular lignocellulosic hydrogen bonds in biomass (Hasanov et al. 2020). Previous studies have proved that pretreatment of RH increases the capability, adsorption capacity, stability, as well as chelating capacity (Acharya et al. 2018). A comparative study of adsorption of Cd ion using untreated and pretreated RH showed that when RH was pretreated with K<sub>2</sub>CO<sub>3</sub> the final material was capable of adsorbing 97% Cd(II) ion, and on the other hand the untreated RH was capable of adsorbing only 33% (Akhtar et al. 2010). Tarley et al. (2004) also reported that alkaline pretreated RH could adsorb 75% of Cd(II) ions compared to the untreated RH which could adsorb only 40% of Cd(II) ions. These studies could prove that pretreatment is important to improve the adsorption efficiency of the RH (Tarley et al. 2004). Few recent methods of chemical treatments followed by extraction of value-added chemical products have been discussed in Table 1.

Table 1 details the various chemical treatments for conversion of RH into useful products. Some of the products (1–13 and 15–24) that are formed from RH after treating them with chemical methods are shown in Fig. 3. Tiwari et al. (2022) reported bioethanol production up to  $32.61 \pm 0.45$  g/L using *Klebsiella oxytoca* ATCC 13,182 (a biological pretreatment), and when beef extract was provided as the nitrogen supplement, bioethanol yield increased to  $43.23 \pm 0.7$  g/L (Tiwari et al. 2022). Peiris et al. (2021) reported removal of K and Cl from RH through washing pretreatment. Even if high amounts of water is used, the hot condensate could be returned after the process which could be a good source of washing medium. On the other hand, the leachate contains K and Cl which can be used as a good fertilizer (Peiris et al. 2021).

Ang et al. (2013) reported a comparative study of pretreatments using acids and showed the decreasing order as below:  $\text{HCl} > \text{HNO}_3 > \text{H}_2\text{SO}_4$ . Rest all reagents ( $\text{CH}_3\text{COOH}$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{NaOH}$ , and  $\text{Ca}(\text{OH})_2$ ) gave less than 1 mg/mL of total reducing sugars (TRSs) (Ang et al. 2013). In alkaline hydrolysis of RH, very low levels of TRS was detected because it hydrolyzed the cellulose and hemicellulose fractionally. Metal impurities, like Fe, Mn, Ca, Na, K, and Mg, were removed during HCl and  $\text{H}_2\text{SO}_4$  pretreatments (Bakar et al. 2016). Gonzales et al. (2017) reported that when cellulase was increased from 0.1 mg to 1 mg/mL, only 8% of  $\text{H}_2$  production occurred indicating that less amounts of cellulase are enough. Organic acids, like butyric (10), propanoic (9), formic (7) and acetic (8), were produced during fermentation.  $\text{H}_2$  was produced via the acetate and butyrate production routes, respectively (Gonzales et al. 2017).

Park et al. (2021) used NaOH and KOH for alkaline leaching and both were compared. It was found that KOH at higher concentrations achieved the saturation in yield, whereas for NaOH the saturation in silica yield was achieved at lower concentrations. Impurities, like CaO,  $\text{K}_2\text{O}$ ,  $\text{SO}_3$ , and MgO, were leached with NaOH treatment and resulted in obtaining silica (Park et al. 2021). KOH activated samples had high specific area and larger pore volumes (Shrestha et al. 2019). Jayapal et al. (2013) reported that NaOH produces more xylan (Jayapal et al. 2013). Klangpetch et al. (2022) reported that 2% NaOH is enough to produce xylooligosaccharides (XOS) under microwave conditions at 25 °C (Klangpetch et al. 2022). However, Khat-udomkiri et al. (2018) reported 12% NaOH and a high temperature of 133.64 °C for XOS production. This study also reported that alkaline pretreatment breaks the ester bonds in lignin and hemicellulose, leading to increased xylan and lignin solubility (Khat-udomkiri et al. 2018). The alkaline and the control treatment gave immobilization up to 23% at 36 h (Trujillo-Ramírez et al. 2022). This same study reported a comparison between acid, alkaline, and untreated RH with respect to immobilization of yeast cells. The maximum

support efficiency occurred in the case of acid which was 44.99% compared to the case of alkaline which was 23.25% at 36 h. The untreated RH gave maximum support efficiency up to 23.43% at 36 h.

Some ILs that are used recently in the valorization of RH are shown in Fig. 4. They are capable of forming bonds with the lignocellulosic materials and hence can help remove the recalcitrant nature of the lignin (Rajamani et al. 2021). There are not many literatures that report ILs to be a solvent for RH valorization. The reason can be that RH has  $\text{SiO}_2$  more than carbohydrates so the capital cost might increase. However, the few literatures available in recent years are reported below. ILs possessing a proton in the cation or bisulfate, dihydrogen phosphate, etc., in the anion are categorized as acidic IL. Acidic ILs are more beneficial compared to the neutral ones as the protonated cation interacts with the lignocellulose.

Wang et al. (2021) reported that 376.55% improvement in the product yield was observed when 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) (25) was used alone compared to the untreated one. However, this study did not use an acidic IL which could have been tested to see the comparative studies, instead HCl was added to this IL (Wang et al. 2021). Zhao et al. (2019) reported that addition of  $\text{FeCl}_3$  to [Bmim][Cl] could convert xylose to give 75% furfural (conversion of xylose = 99% at 140 °C) (Zhao et al. 2019). Liu et al. (2022) used an immobilized IL prepared on a silica carrier named as Imm- $\text{HSO}_4$  (29). This IL could undergo four cycles with good efficiency up to 74.6% furfural from RH. With the addition of  $\text{AlCl}_3$  to the IL, 1-octyl-3-methylpyridinium chloride ( $[\text{C}_8\text{C}_1\text{Py}][\text{Cl}]$ ) (26), the yield of TRS was only 2% higher than what was reported when IL was used alone. This proves that addition of metal was not required to get good conversion and these metal chlorides can be avoided (Liu et al. 2022). Pyridinium-based IL with  $\text{C}_8$  alkyl chain was found to be biodegradable (Docherty et al. 2010, 2015). The dicationic IL, 1,1-bis(3-methylimidazolium-1-yl) butylene hydrogensulfate ( $[\text{C}_4(\text{Mim})_2][2\text{HSO}_4]$ ) (27), is less thermally stable compared to the monocationic IL, 1-butyl-3-methylimidazolium hydrogensulfate ([Bmim][ $\text{HSO}_4$ ]) (28). But the temperature used by Ullah et al. (2019) was only 100 °C and hence the dicationic IL could be used. The dicationic IL was capable of 26% lignin extraction and the monocationic IL was capable of only 16% lignin extraction. This can be due to the higher acidity of the dicationic IL containing two moles of bisulfate anion. The acidic species help break the ether linkage between lignin and hemicellulose moieties, and thus, more lignin can be extracted. The ultrasonication gave higher extraction yields than the corresponding conventional method because of the cavitation induced in the former case which is responsible for the formation of free radicals. These free radicals help in the deconstruction of the lignocellulosic material (Ullah et al. 2019).

**Table 1** Valorization of RH via chemical treatment

S. no	Various chemical treatments	Applications and demerits (if any)	References
<b>Acid treatment</b>			
1	Acid pretreatment followed by fermentation	Cellular retention for acid-treated RH was 98.35 mg g <sup>-1</sup> at 24 h Maximum support efficiency of 44.99% (pretreated with acid) was observed at 36 h Immobilization of yeast cells occurred	Trujillo-Ramírez et al. (2022)
2	Dilute acid pretreatment followed by enzymatic hydrolysis and batch H <sub>2</sub> fermentation	95.74% sugar recovery (glucose (4), xylose (5), arabinose (6)) was observed at 1.0 mg mL <sup>-1</sup> cellulase loading 473.1 mL H <sub>2</sub> g <sup>-1</sup> RH was obtained Also formic acid (7), acetic acid (8), propanoic acid (9), butyric acid (10), levulinic acid (11), furfural (12), 5-HMF (13) were formed between 0.06 and 17.14 g L <sup>-1</sup>	Gonzales et al. (2017)
3	Acid pretreatment followed by thermal treatment	HCl could remove the metallic impurities slightly greater than H <sub>2</sub> SO <sub>4</sub> Amorphous silica was obtained with purity above 99%	Bakar et al. (2016)
<b>Alkaline treatment</b>			
4	Alkaline leaching	89% of silica was obtained Purity of silica increased from 93.1% to 98.5% after alkaline leaching	Park et al. (2021)
5	Pyrolysis followed by alkaline pretreatment followed by leaching of silica and thereafter carbonization	NCM_K showed very good adsorption properties 1726 mg/g of iodine and 608 mg/g of methylene blue (MB) (14) was adsorbed The obtained results were better than that of commercial AC <b>Demerit:</b> Product will become very expensive due to so many processes	Shrestha et al. (2019)
6	Pretreatment followed by enzymatic hydrolysis	54.49 ± 0.31% of xylan (15) was obtained 17.35 ± 0.31 mg XOS (16) per mL of xylan was obtained after enzymatic hydrolysis	Khat-udomkiri et al. (2018)
<b>Other treatments</b>			
7	Pretreatment followed by smoldering <sup>a</sup>	26.6% silica was obtained 4.16% K <sub>2</sub> O, 2.61% CaO, 1.25% SO <sub>3</sub> , 1.15% P <sub>2</sub> O <sub>5</sub> , 1.08% MgO, 0.78% Cl, 0.73% Fe <sub>2</sub> O <sub>3</sub> , 0.72% Al <sub>2</sub> O <sub>3</sub> were obtained <b>Demerit:</b> Smoldering temperature (560 °C) was very high	Yan et al. (2022)
8	Steam pretreatment followed by enzymatic hydrolysis	90.6 g/L of glucose (4) was obtained <b>Demerit:</b> The temperature (218 °C) was very high	Montipó et al. (2021)
9	Washing treatment <sup>b</sup>	75% of Cl and 50% of K were removed at mild temperature (65 °C)	Peiris et al. (2021)
10	Hydrothermal pretreatment in microwave followed by saponification	36.18 ± 1.83 mg/g of lignin (1) content was obtained Phenolic esters (17) <sup>c</sup> , vanillin (18), benzoic acid (19), vanillic acid (20), p-OH-benzaldehyde (21), 8-O-4'-DIFA (22), trans-ferulic acid (23), proto-catechuic aldehyde (24) were obtained <sup>d</sup>	Wu et al. (2018)
11	[Bmim][Cl] (25) + HCl pretreatment followed by enzymatic hydrolysis	At 50 h more than 25% cellulose (2) conversion occurred IL alone gave 5% cellulose conversion <b>Demerit:</b> The amount of IL used was 78 g which is very high. Recyclability and reusability can help making the process economical. Acidic IL can be used instead of adding acids to IL	Liu et al. (2022)
12	[C <sub>8</sub> C <sub>1</sub> Py][Cl] (26) IL treatment	58% of TRS was obtained	Naz et al. (2021)

**Table 1** (continued)

S. no	Various chemical treatments	Applications and demerits (if any)	References
13	$[(C_4(Mim)_2)[2HSO_4]]$ ( <b>27</b> ) IL treatment in ultrasonicator	39% lignin ( <b>1</b> ) extraction was observed 42% levulinic acid ( <b>11</b> ) was obtained <b>Demerit:</b> The amount of IL used was 15 times more than RH taken which was very high. Recyclability and reusability can help in making the process economical	Ullah et al. (2019)

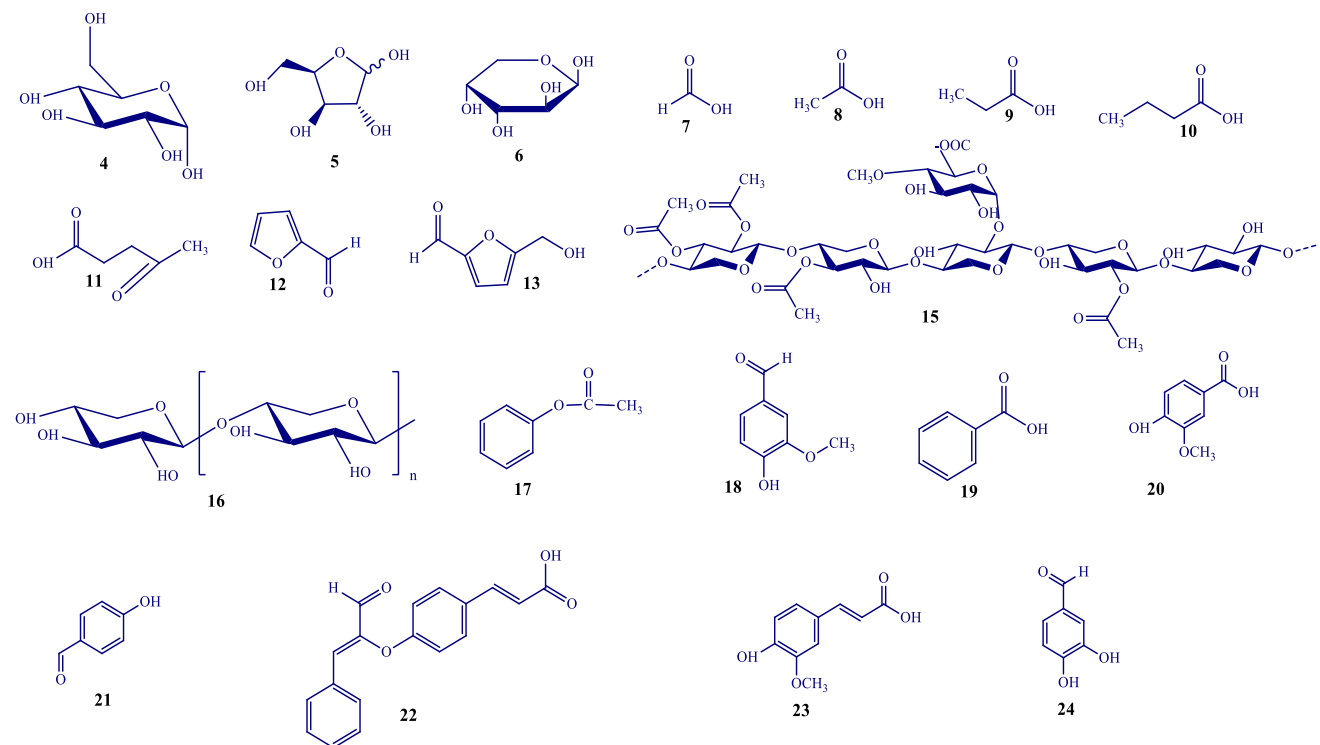
AC activated carbon, BET Brunauer–Emmett–Teller,  $[Bmim][Cl]$  (**25**) 1-butyl-1-methylimidazolium chloride, CBU cellobiase unit  $[C_4(Mim)_2][2HSO_4]$  (**27**) 1,1-Bis(3-methylimidazolium-1-yl) butylene hydrogensulfate,  $[C_8C_1Py][Cl]$  (**26**) 1-Octyl-3-methylpyridinium chloride, 8-O-4'-DIFA (**22**) 8-O-4'-diferulic acid, FPU filter paper unit, MB (**14**) methylene blue, NCM nanoporous carbon material, NCM\_K KOH activated NCM, RH rice husk, RHC rice husk char, TRS total reducing sugar, WIS water insoluble solids, XOS (**16**) xylooligosaccharides

<sup>a</sup>Smoldering is slow flameless burning at reduced temperature

<sup>b</sup>Leaching behavior was studied by measuring the conductance of washed water

<sup>c</sup>The procedure for analysis of phenolic compounds was reported in this study

<sup>d</sup>These quantities were smaller than 5 mg/g

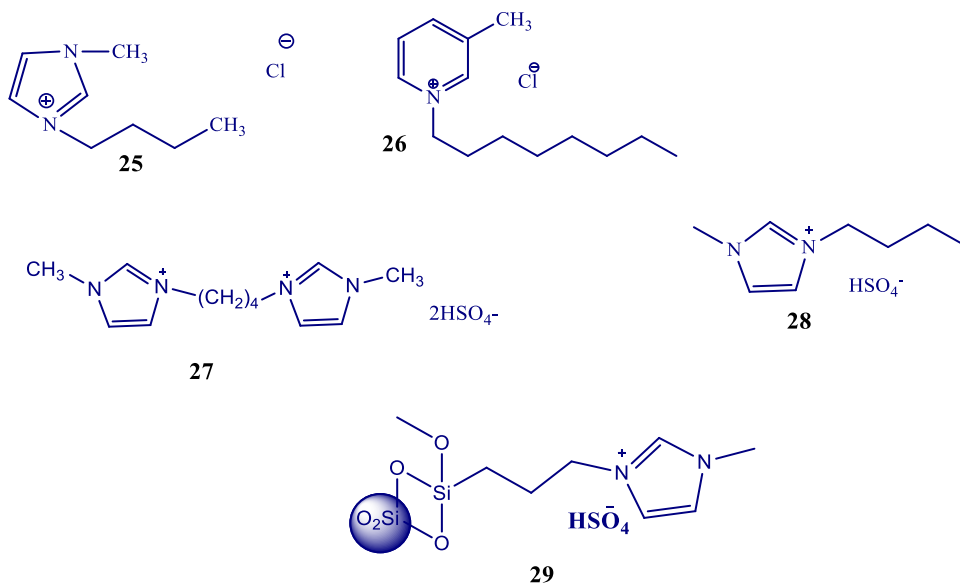


**Fig. 3** Various products obtained from rice husk; **4**: glucose; **5**: xylose; **6**: arabinose; **7**: formic acid; **8**: acetic acid; **9**: propanoic acid; **10**: butyric acid; **11**: levulinic acid; **12**: furfural; **13**: 5-hydroxymethylfurfural; **15**: xylan; **16**: xylooligosaccharides; **17**: phenolic esters;

**18**: vanillin; **19**: benzoic acid; **20**: vanillic acid; **21**: p-OH-benzaldehyde; **22**: 8-O-4'-diferulic acid; **23**: trans-ferulic acid; **24**: protocatechuic aldehyde



**Fig. 4** Ionic liquids used for valorizing rice husk. **25:** [Bmim][Cl] = 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]); **26:** [C<sub>8</sub>C<sub>1</sub>Py][Cl] = 1-octyl-3-methylpyridinium chloride; **27:** [C<sub>4</sub>(Mim)<sub>2</sub>][2HSO<sub>4</sub>] = 1,1-bis(3-methylimidazolium-1-yl) butylene hydrogensulfate; **28:** [Bmim][HSO<sub>4</sub>] = 1-butyl-3-methylimidazolium hydrogensulfate; **29:** ImmHSO<sub>4</sub>-IL = immobilized imidazolium acidic ionic liquid with HSO<sub>4</sub> anion



## RH-based Functional Materials and Their Applications

The additional property of a foreign substance in RH makes it a better material. They have been used as catalysts as well as adsorbents for removing pollutants (metal ions, dyes, drugs, gases etc.). Many methods have been studied for the extraction of pollutants from the environment, such as solvent extraction (Khataei et al. 2022), ion exchange resins (Czupryński et al. 2022), and liquid emulsion membrane (Zaulkiflee et al. 2022). RHA obtained by burning RHs can be further modified by addition of metal oxides to enhance the adsorption and desorption capacities. Release of several amounts of untreated dye waste water from the industries cause serious environmental issues. The toxic and carcinogenic effects of this water cause several hazardous problems to the aquatic life and also human health. Dyes have complex structure, are synthetic in origin, and are highly soluble in water. Hence, it is a challenge to remove dyes from the waste water. The removal of drugs mainly antibiotics from waste water is important because these can cause the microorganisms to become resistant toward them (Yang et al. 2021). The functional materials due to the presence of large surface area can be used as electrode materials as well. Shamsollahi et al. (2019) reviewed RH being used as adsorbents as well as an immobilization system which makes it a functional biocatalyst that could be easily separated and recycled. The benefit of RH is that it is resistant to microbial and fungal attack (Shamsollahi et al. 2019). Table 2 enlists the applications of RH-based functional materials which are produced after addition of metals, non-metals, or their oxides. RH can be added along with metals, non-metals, or their oxides for many applications, such as support for catalysts, removal of metal ions from waste waters, adsorption of organic dyes,

adsorption of metal oxide nanoparticles, adsorption of methane and antibiotics ( $\beta$ -lactam amoxicillin), etc.

Lignocellulosic bio-oils can replace fossil fuels but due to the polymerizing nature of some oxygenates, like furfural (12), make them unstable (Tang et al. 2008; Zhang et al. 2013). For this reason furfurals should be converted to a more stable component by reacting them with acids, like acetic acid (8) to give furfuryl acetate (30) along with a byproduct furfuryl alcohol (31). Mild acidic catalyst should be used because stronger ones may cause polymerization instead of one-pot hydrogenation esterification (OHE). Hashim et al. (2020) reported a catalyst which consists of SiO<sub>2</sub> (derived from RH) along with some metals for OHE reaction (Scheme 2). The catalysts tested in this study gave the following activity order: RHSiO<sub>2</sub>-Cu < RHSiO<sub>2</sub>-Cu-Al < RHSiO<sub>2</sub>-Cu-Al-Mg. The catalyst with the three metals Cu, Al, and Mg showed the best results but even this catalyst lost significant activity after recycling it (Hashim et al. 2020).

Shu et al. (2019) reported that the use of oxides of Mn-Ce on AC derived from RH was selective toward the reduction of NO<sub>x</sub> with ammonia. High chemisorbed oxygen content, high Mn<sup>+4</sup>/Mn<sup>+3</sup> ratios, more Brønsted acid sites and increased redox activity improved the catalytic performance (Shu et al. 2019). Siriworarat et al. (2017) reported CO<sub>2</sub> conversion to methanol. Cu/Zn were loaded together on the MCM-41 support which was used as a catalyst and the promoter was Pd where increase in Pd content increased the amount of methanol. Synthesis of MCM-41 and (F)MCM-41 was carried out using sol-gel method and flame spray pyrolysis, respectively. The former one had larger surface area and agglomeration of metal oxides occurred in case of (F)MCM-41 catalyst (Siriworarat et al. 2017). Another study by Bonura et al. (2014) reported a much higher yield

**Table 2** Applications of recent RH-based functional materials as catalysts, adsorbents, and electrode materials

S No	RH-based functional materials	Operating conditions	Applications and demerits, if any	References
<b>RH-based functional materials as catalysts</b>				
1	RHSiO <sub>2</sub> -Cu-Al-Mg <sup>a</sup>	0.1 g of catalyst, furfural (12):acetic acid (8) (v/v) = 20% in ethanol, 150 °C, 20 bars of H <sub>2</sub> , 4 h <sup>#</sup>	<b>Applications</b> Selectivity to furfuryl acetate (30) was 24.5% Conversion of furfural was above 95% The catalyst was thermally stable. Mg acted as an acidity regulator and helped the catalyst to be selective toward OHE <b>Demerit:</b> The catalyst post-recycling dropped the furfural conversion by ~ 18%, which is mainly due to the leaching of active metal components	Hashim et al. (2020)
2	Mn-Ce/RAC <sup>b</sup>	5 wt% of catalyst, 240 °C, 800 ppm NO, 800 ppm NH <sub>3</sub> , 3% O <sub>2</sub> , N <sub>2</sub> as balance gas, flow rate = 500 mL min <sup>-1</sup> , GHSV = 30,000 h <sup>-1</sup> , 1 h The conversion was also tested in the presence of SO <sub>2</sub> and H <sub>2</sub> O	<b>Applications</b> More than 90% NO <sub>x</sub> conversion and 90% N <sub>2</sub> selectivity High SO <sub>2</sub> tolerance by Mn-Ce/RAC catalyst Selective even at low temperature <b>Demerit:</b> With the simultaneous addition of SO <sub>2</sub> and H <sub>2</sub> O, led to the rapid formation of ammonium sulfate species which further decreased NO <sub>x</sub> conversion by 18%	Shu et al. (2019)
3	15Pd25Cu25Zn/MCM-41 The catalyst can be read as 15% of Pd + 25%Cu + 25%Zn	0.2 g of catalyst + quartz = 1:3, 250 °C, 25 bars, 40 min, H <sub>2</sub> :CO <sub>2</sub> = 3:1, balanced with Ar, flow rate = 40 mL/min, GHSV = 1,800 h <sup>-1c</sup>	<b>Application</b> Space time yield of methanol using 15Pd25Cu25Zn/MCM-41 catalyst was 112 g/kg <sub>(catalyst)</sub> h <b>Demerit:</b> Other study reported a higher space time yield, i.e., 170 g/kg <sub>(catalyst)</sub> h (Bonura et al. 2014)	Siriworarat et al. (2017)
<b>RH-based functional materials as adsorbents</b>				
4	Ni-MCM-41 <sup>d</sup>	Adsorbent dosage = 50 mg, initial concentration of rhodamine dye (32) = 5 mg/L, ambient temperature, contact time = 24 h, 5 mL H <sub>2</sub> O <sub>2</sub> , 9.2 mL acetonitrile as solvent <sup>#</sup>	<b>Applications</b> The maximum conversion of rhodamine (32) reached 95.98% 94% reduction in the cost of MCM-41 can be obtained by using this method to prepare Ni-MCM-41 compared to mesoporous silica which is bought commercially <b>Demerit:</b> The tests were carried out only in acetonitrile and not in aqueous solutions	Niculescu et al. (2021)
5	RH-GO/SBA-15	Adsorbent dosage = 5 mg, initial concentration of dye = 50 mg/L, pH = 2, contact time = 75 min, amount of GO suspension = 6 g <sup>e</sup>	<b>Application</b> Adsorption of MB (14) reached 456.63 mg/g <b>Demerit:</b> The MB removal was efficient at low pH = 2, but this catalyst was not efficient enough when pH was increased to 6. At higher pH, degradation of pore structure occurs and due to this adsorption decreases	Liou et al. (2021)

Table 2 (continued)

S No	RH-based functional materials	Operating conditions	Applications and demerits, if any	References
6	CeO <sub>2</sub> @SiO <sub>2</sub> <sup>f</sup>	Adsorbent dosage = 10 mg/mL, initial concentration of AMX (33) <sup>g</sup> = 2.5 mg/L, pH = 3, contact time = 120 min, 25 ± 2 °C, 1 mM KCl	<p><b>Applications</b> AMX (33) adsorption using CeO<sub>2</sub>@SiO<sub>2</sub> reached 12.5 mg/g with almost 100% adsorption efficiency Organics present in the water did not show much effect on AMX (33) removal Catalyst reusability studies showed that AMX (33) removal was still higher than 74% even after 4<sup>th</sup> stage</p> <p><b>Demerit:</b> At higher pH, the AMX adsorption reduced due to the negative charge formed on AMX beyond pH 7.5. Hence, there will be competition between the OH<sup>-</sup> ion and AMX for the adsorption</p>	Pham et al. (2021)
7	GO/OMC	Adsorbent dosage = 5.0 mg in 250 mL of MB (14) solution, initial dye concentration = 10–20 mg/L, 25°C, pH = 7, contact time = 270 min <sup>#</sup>	<p><b>Application</b> The dye adsorption using GO/OMC reached 1591 mg/g with 100% dye removal efficiency</p> <p><b>Demerit:</b> Highly acidic pH allowed competition of H<sup>+</sup> ions with MB adsorption, leading to decreased adsorption of the dye. This catalyst works best only at neutral pH</p>	Liou et al. (2020)
8	Fe <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> <sup>f</sup>	Adsorbent dosage = 0.5 g/L, initial tartrazine (34) dye concentration = 50 mg/L, 12 mM H <sub>2</sub> O <sub>2</sub> , 30 °C, pH = 3.0, contact time = 80 min, 100 mL of dye solution <sup>#</sup>	<p><b>Application</b> Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> showed the best performance and has great potential for the removal of tartrazine (34) dye up to 98.5%</p> <p><b>Demerits:</b> pH lower than 2.5 led to decreased performance because there is a competition between H<sup>+</sup> ions and tartrazine dye adsorption. Thus, this catalyst cannot be used for alkaline waste water. This catalyst showed higher aggregation</p>	Vu et al. (2019)
9	RH+FeO	Adsorbent dosage = 2.5 mg/L, amount of metal = 10 mg/L, stirred at 250 rpm, 30 °C, pH = 6, contact time = 60 min	<p><b>Applications</b> Arsenic (III) ion adsorption using RH+FeO reached 82 mg/g with 95% adsorption efficiency Up to 56% of arsenic was removed in 5<sup>th</sup> stage</p> <p><b>Demerit:</b> Arsenic removal decreased in the basic medium because negative arsenic ions and hydroxide ions repel each other in higher pH</p>	Pillai et al. (2020)

Table 2 (continued)

S No	RH-based functional materials	Operating conditions	Applications and demerits, if any	References
10	50%Cu-10%Ce/SiO <sub>2</sub> <sup>f</sup>	Adsorbent dosage = 10 mg, the flue gas condition was 200 ppm NO, 200 ppm NH <sub>3</sub> , 6% O <sub>2</sub> , 300 °C and space velocity of 3600 h <sup>-1</sup> , contact time = 900 min	<b>Applications</b> Up to 85% of NO removal occurred Recycled copper ions from panel industry wastewater were used for the synthesis of catalyst <b>Demerit:</b> The temperature of adsorption is high	Chen et al. (2019)
11	50%Cu/SiO <sub>2</sub> <sup>f</sup>	Adsorbent dosage = 10 mg, inlet Hg <sup>0</sup> concentration = 65 µg/m <sup>3</sup> , 150 °C, contact time = 900 min	<b>Applications</b> 50%Cu/SiO <sub>2</sub> exhibited 7769.9 mg/g adsorption, i.e., the total Hg <sup>0</sup> removal efficiency reached 90.2% Copper ions generated from effluent water were used for the synthesis of the catalyst <b>Demerit:</b> On increasing the inlet Hg <sup>0</sup> concentration to 100 µg/m <sup>3</sup> , the adsorption efficiency decreased to 63.1% which may be due to the absence of active vacant sites	
12	MgO-BCR	Adsorbent dosage = 0.2 g, 200 mL of 100 mg/L Cd (II) solution, stirred at 160 rpm, 25 °C, pH = 5, contact time = 120 min	<b>Application</b> Cd (II) ion adsorption using MgO-BCR reached 18.8 mg/g compared to BCR alone which was 6.36 mg/g <b>Demerit:</b> At higher pH the adsorption decreases owing to the formation of precipitates of hydroxide complexes	Xiang et al. (2018)
13	RHA-alumina composite	Adsorbent dosage = 0.1 g, 10 mL of 120.6 mg/L uranium (VI) solution, 25 ± 2 °C, pH = 5, contact time = 60 min <sup>#</sup>	<b>Application</b> Uranium (VI) ion adsorption reached 68 mg/L with 96.35% efficiency <b>Demerits:</b> At low pH, the adsorption decreases due to the competition between the H <sup>+</sup> ions and uranium ions Also in the presence of other positive ions, the adsorption of uranium decreased due to the absence of active vacant sites	Youssef et al. (2018)
<b>RH-based functional materials as electrode</b>				
14	ZnO/RHC	<b>Electrodes:</b> Counter and reference electrodes were metallic lithium material. Working electrode was active material: acetylene black: PVDF = 8:1:1 <b>Electrolyte:</b> 1.01 M LiPF <sub>6</sub> electrolyte (0.14 mL) in EC:DMC (v/v) = 1:1	<b>Applications</b> Reversibility studies showed specific capacity of 1002.5 mA h g <sup>-1</sup> after 160 cycles at 0.2 C This was higher than the theoretical specific capacity of ZnO (978 mA h g <sup>-1</sup> ) <b>Demerit:</b> The flower-like structure of the material was one of the benefits for good efficiency but after repeated cycles it was found to be damaged	Li et al. (2020)
15	SnO <sub>2</sub> @RH-SiO <sub>2</sub> <sup>f</sup>	<b>Electrodes:</b> Counter electrode was Pt wire and the reference electrode was Ag/AgCl. Working electrode was active material: PVDF: carbon black = 8:1:1 <b>Electrolyte:</b> 0.5 M Na <sub>2</sub> SO <sub>4</sub>	<b>Application</b> Specific capacitance of SnO <sub>2</sub> @RH-SiO <sub>2</sub> composite was observed to be 448 F/g with current density of 1 A/g <b>Demerit:</b> On increasing the current, the specific capacitance decreased which may be due to poor electrochemical reaction at high current density	Vijayan et al. (2020)

Table 2 (continued)

S No	RH-based functional materials	Operating conditions	Applications and demerits, if any	References
16	RH-derived carbon@SnO <sub>2</sub> @rGO <sup>b</sup>	<b>Electrodes:</b> Counter electrode and the reference electrode were lithium foil Working electrode was active material:PVDF:carbon black = 8:1:1 <b>Electrolyte:</b> 1 M LiPF <sub>6</sub> in EC:DEC (w/w) = 50:50	<b>Application</b> Reversibility studies showed specific capacity of 1206.9 mAhg <sup>-1</sup> after 100 cycles at 0.2 C <b>Demerits:</b> The material was flaky due to superimposition of other materials on it during charging and discharging of the material there was change in volume leading to its damage	Shuqi et al. (2020)
17	RHAC/NiCo <sub>2</sub> S <sub>4</sub> <sup>i</sup>	<b>Electrodes:</b> Counter electrode was platinum filament and the reference electrode was standard calomel electrode Working electrode was active material:acetylene carbon black:PTFE = 8:1:1 <b>Electrolyte:</b> 2.0 M KOH	<b>Application</b> Reversibility studies showed specific capacity up to 86% after 5000 cycles at 1 A/g <b>Demerit:</b> At low carbon content agglomeration occurred	Wang et al. (2019)
18	C/SiO <sub>2</sub> <sup>f</sup>	<b>Electrodes:</b> Counter electrode was pure lithium metal foil. Reference electrode was not mentioned Working electrode was active material: acetylene black/binder:PVDF = 8:1:1 <b>Electrolyte:</b> 1 M LiPF <sub>6</sub> in EC/DEC/DMC (1:1:1 v/v/v)	<b>Application</b> LIBs could maintain good reversibility cycles within a current density of 100 mA g <sup>-1</sup> <b>Demerit:</b> The material was synthesized at high temperature, like 800 °C	Guo et al. (2020)
19	ZnO/CoO@RHC <sup>j</sup>	<b>Electrodes:</b> Counter and reference electrode were not mentioned Working electrode was active material:acetylene black: PVDF = 8:1:1 <b>Electrolyte:</b> It was not mentioned	<b>Application</b> Reversibility studies showed specific capacity 972 mAh g <sup>-1</sup> over 150 cycles at 100 mA g <sup>-1</sup> <b>Demerit:</b> Decomposition of the material occurred after repeated cycles	Yu et al. (2019)

AC activated carbon, ACP H<sub>3</sub>PO<sub>4</sub> activated carbon, ACZn ZnCl<sub>2</sub> activated carbon, AMX β-lactam amoxicillin, BCR rice husk biochar composite, BET Brunauer–Emmett–Teller, DEC diethyl carbonate, DMC dimethyl carbonate, EC ethylene carbonate, GHSV gas hourly space velocity, GO graphene oxide, LIB lithium ion battery, MB methylene blue, NMP N-methyl-2-pyrrolidone, OHE one-pot hydrogenation and esterification, OMC ordered mesoporous carbon, PTFE polytetrafluoroethylene, PVDF polyvinylidene fluoride, RH rice husk, RHA rice husk ash, RHAC rice husk activated carbon, RHC rice husk-derived carbon, SBA-15 Santa Barbara Amorphous-15

<sup>a</sup>The catalyst had slit-shaped pores

<sup>b</sup>RAC = AC extracted from rice husk

<sup>c</sup>The catalyst was reduced initially with hydrogen so that the total hydrogen used as the reactant should not end up reducing the catalyst

<sup>d</sup>MCM-41, type mesoporous silica was obtained from rice husk through various modifications and “-r” stands for rice husk. MCM-41<sub>r</sub> is impregnated into aqueous solution of nickel acetate

<sup>e</sup>Temperature and the stirring rate per minute are not available. All the other parameters have been taken from the plots given in this study

<sup>f</sup>SiO<sub>2</sub> was obtained from rice husk

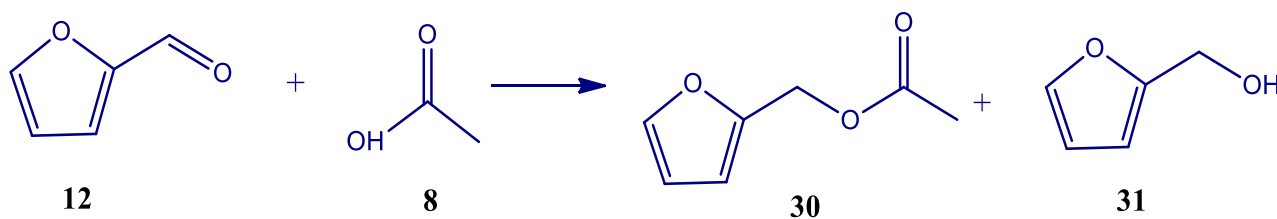
<sup>g</sup>AMX solutions were obtained after centrifugation at 12,000 rpm at 5 °C for 15 min

<sup>h</sup>Rice husk-derived carbon@SnO<sub>2</sub>@reduced graphene oxide (rGO)

<sup>i</sup>Activated carbon derived from gasified rice husk carbon (RHAC)

<sup>j</sup>Zinc-cobalt bimetallic oxides supported on the carbon matrix derived from RH

<sup>#</sup>rpm not mentioned for these entries



**Scheme 2** Conversion of furfural to the corresponding furfuryl acetate (**30**) and furfuryl alcohol (**31**)

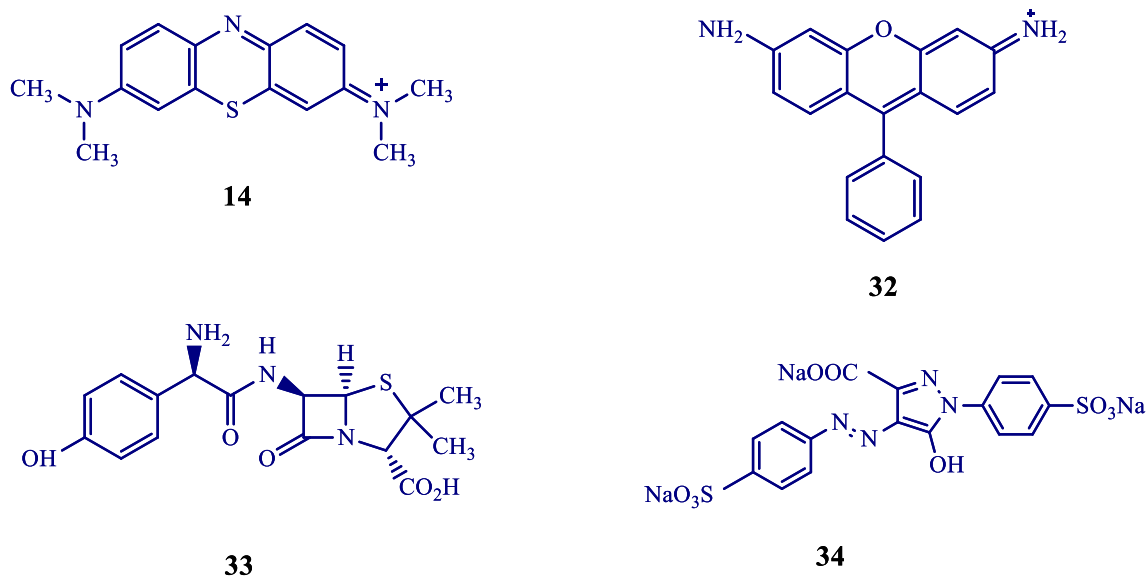
of methanol from CO<sub>2</sub>, but the pressure was almost three times higher than that used in Siriworarat et al. 2017.

Nanoparticles (NPs) due to their large surface area and their capacity to adsorb toxins from water are being widely used as adsorbents. Heavy metals are non-biodegradable and can bioaccumulate, which would pass through the food chain and in turn cause serious diseases and disorders. Although AC is a good adsorbent, it is costly and there is loss in regeneration; therefore, RHA which is easily available in huge amounts can serve as an effective bio-adsorbent. Arsenic arises due to natural and anthropological activities which may lead to severe health conditions, such as skin cancer, lungs and brain damage, intestine irritation, and decreased levels of red and white blood cells formation. Arsenic is widely used in many industries, such as textiles, alloying agents, metal adhesives, wood preservatives, pesticides, etc. FeO being cheap, easily available, and having high affinity than any other metal oxide is being used either singly or as a mixture of FeO with another adsorbent (Chai et al. 2013). It was observed that the magnetic property of FeO NPs helps it bind arsenic ions through electrostatic attraction and

due to this property it can be recovered easily (Pillai et al. 2020). Xiang et al. (2018) reported removal of cadmium ions which is present in waste waters of industries and is highly toxic. Non-toxic and eco-friendly MgO is impregnated on RH biochar which could enhance the removal of Cd (II) ions from waste water (Xiang et al. 2018). RHA-alumina composite was capable of removing uranium (VI) ions (Youssef et al. 2018).

Coal-fired power plants release huge amounts of Hg which shows long retention time in the environment leading to acid rains and formation of photochemical smog (Zhang et al. 2017). Hg<sup>0</sup> due to its high stability is hard to be removed from the environment. Chen et al. (2019) used copper ions recycled from panel industrial waste water which were incorporated into RH-derived silica particles via the silicate-exfoliation method. This material could successfully remove Hg<sup>0</sup>. The coal-fired power plants also release out NO<sub>x</sub> and the incorporation of Cu and Ce oxides in RH-derived silica led to efficient removal of NO (Chen et al. 2019).

Organic dyes and pharmaceutical drugs have complex aromatic structures which are being released into the water



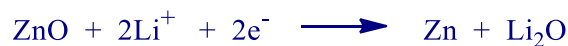
**Fig. 5** Structure of some adsorbents. **14**: methylene blue; **32**: rhodamine dye; **33**: β-lactam amoxicillin; **34**: tartrazine dye

bodies that cause severe pollution. Some pollutants of these kind are shown in Fig. 5. Methylene blue (MB) (**14**) is one of the most widely used dye in the industries (Tang et al. 2021). Graphene oxide (GO) being highly hydrophilic in aqueous media leads to filtration difficulty due to its aggregation. Hence, GO cannot be used alone (Liou et al. 2021). Therefore, a meso-structural material Santa Barbara amorphous-15 (SBA-15) that has hexagonally packed uniform porosity, increased surface area, and adjustable pore size is being utilized to increase adsorption capacity by facilitating GO dispersion. SBA-15 is an excellent source for producing ordered mesoporous carbon (OMC) (Liou et al. 2020). Both the studies carried out adsorption for MB removal and the one containing OMC was capable of removing 100% of MB dye (Liou et al. 2020). Van der Waals, electrostatic, and  $\pi$ - $\pi$  binding might be the key reasons for the greater adsorption capacity of RH-GO/SBA-15 because of the interaction between MB dye (cationic) and the adsorbent (anionic). The adsorbent is anionic mainly due to negatively charged oxygen-containing functional groups, like epoxy, hydroxyl, and carboxyl (Liou et al. 2021). Ni-MCM-41 exhibited higher catalytic activity than Fe-MCM-41 adsorbent for rhodamine dye (**32**) (Niculescu et al. 2021). Tartrazine dye (**34**) was also removed using RH-based catalyst (Vu et al. 2019).

It is well known that rare earth oxides, such as cerium oxide exhibit unique properties, like adsorption capacity and as catalyst (Gangopadhyay et al. 2014). However, CeO<sub>2</sub> being a costly material compared to other metal oxides is the major disadvantage, so silica was combined with CeO<sub>2</sub> to get a useful adsorbent. However, it was observed that  $\beta$ -lactam amoxicillin (AMX) (**33**) leads to severe problems in antibiotic resistance genes (Pham et al. 2021).

RH-based functional materials were also used as electrodes. The presence of SnO<sub>2</sub> provided reactive surfaces for the adsorption and desorption of charges. Because of this the charge storage was possible and SnO<sub>2</sub>@RH-SiO<sub>2</sub> could act as a supercapacitor (Vijayan et al. 2020). SnO<sub>2</sub> nanoparticles (SnO<sub>2</sub> NPs) and carbon chain of RH form strong chemical bonds due to which the leaching of SnO<sub>2</sub> NPs did not occur during cycling. These characteristics make it an effective anode material for LIBs (Scheme 3). The same material when added with reduced graphene oxide (rGO) was called as RHC@SnO<sub>2</sub>@rGO. During the cycle there was a slight fluctuation which was due to the change in the volume of the material during charging and discharging causing damage or breakage of the material (Liang et al. 2020). C/SiO<sub>2</sub> in which SiO<sub>2</sub> was produced from RH was used in LIBs. RH was decomposed and the sp<sup>2</sup> hybridized carbon in oxygen functional groups significantly disappeared. This carbon was arranged in a honeycomb structure which enhanced the stability of the material (Guo et al. 2020). Bimetallic oxides without RH show limited rate performance and reduced cycle stability.

Discharge process:



Charge process:



**Scheme 3** Charging and discharging reactions in a LIB (Li et al. 2020)

In the presence of RH, the bimetallic oxide ZnO/CoO NPs showed increased conductivity, cycle stability, as well as reversibility (Yu et al. 2019).

Strong interaction between Zn and carbon coating of RH contributed to good reversible capacity and cycle stability of ZnO/RHC. The flower-like structure allowed in seepage of electrolytes (Li et al. 2020). The efficiency of NiCo<sub>2</sub>S<sub>4</sub> material increased because the mesopores facilitated seepage of electrolyte, thereby reaching more electroactive sites (Wang et al. 2019).

## Conclusion

This literature review highlights the importance of RH as such, RH-based or RH-derived materials and different useful chemicals obtained from it. The transformation of agro waste biomass, such as RH, which is obtained at the end of each harvesting cycle into useful materials has become an important aspect of agriculture economy. All the studies discussed in this review prove that RH can be transformed into a number of useful materials or chemicals with simple treatments. The reports on valorization of RH proves it as an important material in the agriculture related circular economy making it a valuable agricultural waste or biomass. Importantly, the RH-derived materials and chemicals are found to be less expensive than those obtained from other sources. A list of chemicals derived from RH include sugars, aromatic esters, carboxylic acids, etc., and all these chemicals have synthetic value. Bioethanol is also a noticeable

product that can be used in number of different applications. Continued research on valorization of RH would help in obtaining new and better chemicals or products with higher yields which can be applicable in different technological fields.

Although extensive research has been carried on RH and RH-derived materials or chemicals and the list of products that can be obtained from RH has increased, there still exist some limitations and challenges related to RH. The process developments for some of the very useful materials or products obtained from RH are needed. Most of the recent reports and applications tested include only the potential applications of the materials obtained or deal with lab-scale testing or small-scale production of RH-derived chemicals. Large-scale production of some RH-derived materials can be carried out by taking the lab-scale finding to the next level by considering other engineering aspects and costs associated with the processes. This may also give rise to further small-scale industries that will process the RH biomass into useful products or materials. This will provide another profit-making option to the farmers who produce and discard a huge quantity of RH every year. Therefore, there is still scope for further research in the process development aspect of transformation of RH into valuable chemicals or materials. Increasing the yield of useful chemicals obtained by proper choice of chemical treatments or solvents is another challenge. The choice of chemical treatment and optimization of the treatment must also be taken into consideration to make the whole process economical. These challenges are wide open, further systematic, and planned research can solve them.

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## Declarations

**Conflict of interest** The authors declare that there is no conflict of interest.

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