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REVIEW PAPER

A review on recent advances in the comprehensive application of rice husk ash

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Abstract Rice husk ash, which is rich in non-crystalline silica, is a by-product material obtained from the combustion of rice husk. Because rice husk ash is available abundantly at a throw-away price with the large specific surface area and the high reaction activity, it is deemed a valued material, which has demonstrated significant influence in not only improving the development of industrialization but also in keeping the environment free from pollution. This paper presents a comprehensive overview of the work carried out on the use of rice husk ash as pozzolanic material, an adsorbent, as well as a source of silica.

Keywords Rice husk ash · Pozzolanic material · Adsorbent · Silica

Introduction

Nowadays, along with the growing demand for energy of society, looking for a renewable and alternative energy resource generally become an inevitable trend, whether in the industrial countries or in the developing countries, where rapid economic development is necessary. From 2001 to 2015, global energy consumption is expected to have grown by 58 %, an increase from 404 quadrillion kW to 640 quadrillion kW [1]. Therefore, there is an ever-increasing interest in utilizing waste materials worldwide, which, at the same time, conforms to the dominant development direction of the industry, which is a green economy and low-carbon environment protection.

Rice, which provides a major source of food for billions of people, covers 1 % of the surface of the earth. Rice hull (RH), the outer covering of paddy rice, is an

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important by-product during the milling process and residue ash is generated after the burning of RH and the ash is called rice husk ash (RHA), which is a primary waste material in the agricultural industry. Globally, the annual output of rice paddy is approximately 600 million tons, of which 95 % is produced by 20 countries [2]. Assuming the ratio of a husk to paddy was approximately 20 % [3] and the ratio of an ash to husk was approximately 18 % [4], this also means approximately 22 million tons of RH is produced and about 6.4 million tons of RHA is generated in China alone. So large amounts of RHA become refuse, and may not be available at all, and it is also a big problem to get rid of it [5].

The typical chemical composition and physical properties of RHA are listed in Table 1 [6–12]. It can be observed that RHA is abundant in silica (SiO_2), and the color changes at different calcination temperatures taking place in RHA of which the color is black mixed with some gray or white particles at different degrees. The black particles represent the carbon with incomplete combustion in RHA [13]. Xu [9] had concluded that RHA had three layered structures: inner, outer, and interface with interstitial and honeycombed pores, which were in fact the major cause for the high chemical activity and large specific surface area of RHA, which meant that RHA had a certain reaction activity. If RHA is utilized, it can not only solve the problem of waste disposal but also keep the environment free from pollution. Therefore, the present review is aimed at summarizing the application of RHA in different areas.

The application of RHA in building materials

Of all the agricultural wastes, RHA, which contains the highest content of silica, is commonly currently regarded as a pozzolanic material [14]. Malhotra and Metha [15] described pozzolanas as siliceous or siliceous and aluminous materials that

Table 1 Chemical composition and physical properties of RHAs

RHA sample	1	2	3	4	5	6	7
SiO_2 (%)	92.40	94.60	87.86	91.71	86.98	87.3	87.2
Al_2O_3 (%)	0.30	0.3	0.68	0.36	0.84	0.15	0.15
Fe_2O_3 (%)	0.40	0.3	0.93	0.90	0.73	0.16	0.16
CaO (%)	0.70	0.40	1.30	0.86	1.40	0.55	0.55
MgO (%)	0.30	0.30	0.35	0.31	0.57	0.35	0.35
Na_2O (%)	0.07	0.20	0.12	0.12	2.46	1.12	1.12
K_2O (%)	2.54	1.30	2.37	1.67	–	3.68	3.68
Loss on ignition	2.31	1.80	–	3.13	5.14	8.55	8.55
Specific gravity (g/cm^3)	2.10	2.05	–	–	2.10	2.06	2.06
Fineness: passing 45 μm (%)	–	98.20	–	–	–	99.00	99.00
Mean particle size (μm)	7.40	7.15	–	0.15	7.40	–	–
References	[6]	[7]	[8]	[9]	[10]	[11]	[12]

possess little or no cementitious property themselves, but would finely disperse and react with calcium hydroxide when water appeared to form compounds with cementing property at ordinary temperature. It was not new to research the application of RHA, which was obtained from burning RH in concrete. As early as 1924, the use of RHA in concrete was reported [16]. Until 1972, many researchers were interested in utilizing ash obtained from uncontrolled combustion. Mehta [12, 17] researched pozzolanic activity of RHA derives from the process of pyroprocessing and made sure that burning RH under controlled incineration conditions could produce RHA, which was rich in amorphous silica. Pitt [18] found that highly pozzolanic RHA could be received when the burning temperature and the residency time were controlled. Since then, several countries have attempted to produce and make use of RHA, including China, Thailand, India, Japan, Guyana, Malaysia, Senegal, Uruguay, and the UK [19–29]. Furthermore, as a mineral admixture for concrete [30–33], RHA could substitute the more expensive cement, which not only lowered the construction cost but also made an important contribution to the low cost of construction materials and consequently enabled people to afford housing. RHA was not just a cheap alternative, meanwhile, it had also been used to improve the property of cementitious products [34–38]. In recent years, several researchers around the world have continued to further improve the pozzolanic activity of RHA.

Qingge [6] described the pozzolanic reactivity of RHA via the pretreatment of hydrochloric acid. Compared with the ash received from heating no pretreatment RH (ORHA), it was shown that the pozzolanic activity was not only stabilized but also enhanced by using hydrochloric acid pretreatment of RH (ARHA); the sensitivity of the pozzolanic reactivity of the ARHA to combustion conditions was decreased. The pozzolanic reactivity of ARHA was almost unaffected by the change of maintaining time whose range had been enlarged in this test, while the pozzolanic reactivity of ORHA had been greatly affected by the maintaining time. Furthermore, in two kinds of RHAs, the amount of silica in amorphous form and the specific surface area could perfectly explain the variation of pozzolanic properties of RHA after pretreating by hydrochloric acid, which was a high amount of amorphous silica and a low specific surface area that led to the pozzolanic properties to decrease. Then added two kinds of RHAs into lime respectively, they both showed a very rapid reaction rate during the initial period. Whereas if the lime consumption of the samples was completed, ARHA need 72 h, and ORHA need 168 h, which meant the reaction rate of ARHA with lime was faster than that of ORHA. The mechanism of the reaction was consistent with diffusion control and the main reaction product was C–S–H gel. This was in agreement with the conclusions of Yu et al. [39]. Compared to the pure cement, the cement blended with ARHA or ORHA possessed faster exothermic rate of hydration, especially the ARHA. And the pore size of the mortar blended with ARHA tended to decrease. As a result, the RHA by hydrochloric acid pretreatment was a valuable pozzolanic material.

Nair [40] investigated the effect of incineration conditions on the structure and properties of RHA formed by burning RH. The loss on ignition and the amount of soluble silica in different samples indicated that the RH burnt at 500 or 700 °C for 12 h was favored to produce reactive RHA, which agreed with the findings of Mehta [17] and Hamad et al. [41] who had identified that the optimum temperature to form reactive ash was at the range of 500–700 °C, although very discrepant reaction time had been suggested. These analyses furthermore showed that not all of the carbon was removed from the samples burnt at 300 °C and the first crystalline silica in the samples appeared at process temperatures of 900 °C or higher. The samples with good pozzolanic index were formed at 500 or 700 °C, especially at 500 °C, which was verified by electrical conductivity tests. So it was concluded that the most reactive RHAs were prepared at 500 °C for 12 h, then directly taking the samples out of the oven and quickly cooling the sample down.

In a separate paper, Nair [42] compared the reactive pozzolanic properties of RHA samples prepared from different types of ovens. They successfully prepared five types of ash samples: RHA collected from annular oven burning (RHA A), RHA obtained from brick oven burning (RHA B), RHA obtained from pit burning (RHA C), RHA received from laboratory oven, that is burning in a muffle furnace (RHA D) and the ash directly obtained from a rice produces mill where RH was used as the fuel (RHA E). They then concluded that RHA samples with higher specific surface area and lower values of loss on ignition could lead to relatively higher pozzolanic activity produce, which was completely consistent with the view of Qingge [6]. However, the presence of un-burnt carbon might damage the effect on the reactivity though it contained abundant silica with amorphous form. The order of the pozzolanic index of these five samples was $E < C < B < A < D$. Hence, two of the important parameters that affect the pozzolanic activity of RHA were the duration and type of combustion, and another important factor for cutting down the content of carbon in ashes was the existence of sufficient oxygen during combustion, which could be explained by RHA C. In addition, the geometry of the burner, the heating rate, etc., also influenced the pozzolanic activity of RHA. The researchers added these RHAs into lime to test their performance in practical application, and the results indicated that RHA put to use as pozzolanic material into construction industry was economic as well as excellent properties.

Ganesan [43] added RHA into cement, whose objective was to investigate RHA as the supplementary cementitious material and permeability properties of concretes and determine the most suitable replacement. The results showed that when reburnt at 650 °C for a period of 1 h, the RHA could transform itself into an efficient pozzolanic material containing 87 % of amorphous silica and a relatively low loss on ignition value. The content of RHA perfectly added into cement without any disadvantageous effect on the strength of concrete was up to 30 %. Meanwhile, replacement with 30 % of reburnt RHA leaded to the permeability properties of concrete have significantly improved, which might be due to the few unburnt carbon in the RHA, that was water permeability fell by approximately 35 %, chloride diffusion fell approximately 28 %, and chloride permeation fell approximately 75 %. The investigations had directly bore on the durability of reinforced concrete constructions, which was causing a long life for the materials.

Givi [8] evaluated the effect of RHA particle size on the workability, water permeability, and strength of concrete. The results revealed that compared to the concrete without RHA, the concrete blended with RHA had higher compressive strength at 90 days. It was also found that RHA could advantageously substitute for cement, and the maximum limit could be up to 15 and 20 %, respectively, by average particle sizes of 95 and 5 μm. Nonetheless, the optimal amount of substitution replacement of RHA for both average particle sizes was 10 %. With an average particle size of 5 μm, the concrete blended with RHA had declared a significant decrease in the coefficient of water absorption, the velocity of water absorption, and the amount of water absorption at all stages. However, with average particle size of 95 μm, the concrete blended with RHA had declared a decrease in water permeability after moisture curing for 90 days. RHA with two kinds of particle size could be conducive to the workability of fresh concrete. Usually, typical concrete mixtures need to mix a mass of water [44]. Other researchers [45, 46] have reported that concrete blended with high-volume fly ash could reduce up to 20 % requirement of water, whereas in the current study, RHA concrete mixtures in particular with the coarser average particle size consumed the water less than fly ash concrete mixtures. The reason of this water requirement reduction was attributed to the sorption of RHA via the oppositely charged surfaces of cement particles and their strong repulsive forces, which does not allow them to flocculate. Thus, the particles of cement were perfectly dispersed and could capture a great number of water which led to the water demand of the system reduced to an acceptable consistency. In consideration of the particle size, the results of this study indicated that the workability of RHA with a particle size of 95 μm was more efficient than 5 μm, which was caused by the high specific surface of RHA particle size of 5 μm resulted in water requirement increasing. Ultimately, it was found that the concrete replaced by 10 % of RHA with particle size of 5 μm possessed less water permeability, high value of compressive strength, and acceptable workability; it was therefore regarded as an optimum formulation.

Producing RHA with highly pozzolanic activity was usually in a fluidized bed furnace, which was developed by Pitt [18]. Whereas Nehdi [7] intended to research pozzolanic RHA obtained from Egyptian RH through a new technology based on a Torbed reactor, which was the first attempt in such production, whereas used in several other applications previously, such as food, soil and sediment remediation, gas scrubbing, catalyst and mineral processing, and removal of volatiles from solids. The new technology successfully produced highly reactive RHA whose performance was similar to silica fume (SF) and RHA prepared in a fluidized bed in the USA. The RHA prepared by the new technology, which was a perfect alternative for SF, needed much less grinding time and much lower content of carbon than that prepared by fluidized bed technology and did not have a substantial increase in the water requirement and the superplasticizer demand. Furthermore, the pozzolanic index of RHA was up to 117 % on the 7th day and 144 % on the 28th day. Compared to SF concrete, RHA concrete obviously improved the compressive strength as high as 40 % on the 56th day, reduced the rapid chloride penetrability, and was more efficient in resisting surface scaling due to deicing salts. It seemed that this new technology could be suitable to prepare highly effective supplementary cementing materials in rice-production countries.

Ramadhansyah [47] studied the effect of different grinding times on the pozzolanic activity and thermal analysis of RHA. They revealed that the less the weight loss, the more the crystalline RHA formed in the process of burning RH. The RHA with the highest pozzolanic activity index appeared when the grinding time lasted 90 min. There was also a significant drop in the pozzolanic activity, which was attributed to the large specific surface area of RHA when the grinding time changed from 90 to 300 min. At the same time, they also indicated that there was no obvious distinction in chemical compositions of RHA with different grinding times. Gemma [48] studied the strength development of concrete with RHA. Compared to concrete without RHA, the concrete blended with RHA possessed much higher compressive strength on the 91st day; this conclusion was amazingly similar to Givi [8], and in the early days, residual RHA performed an advantageous role in the compressive strength of concrete, but it was more significant to control the process of burning RHA to obtain better behavior of the concrete with RHA in the long run. The increase in compressive strength of the RHA concrete was mainly attributed to the pozzolanic activity. The stabilization of residual soil with cement and RHA was studied by Basha et al. [49]. The investigation included that either solely or mixed with cement, the RHA could potentially stabilize the residual soil, and 15–20 % of RHA and 6–8 % of cement were recommended as an optimum amount.

RHA as the source of SiO_2

Silica was a basic raw material that was widely used in many ways, such as in ceramics, chromatograph column packing, adhesives, detergents, electronics, pharmaceuticals, and vegetable oils [50–53]. The conventional approach for preparing silica powders generally employed sodium silicate with acid, while sodium silicate was at present manufactured by smelting quartz sand with sodium carbonate at the temperature as high as 1300 °C in industry [54]. RHA, an industrial residue obtained from the process of burning RH, contained over 60 % of silica in amorphous formation and exhibited high activity [55–57]. Consequently, RHA could be an economically viable raw material for preparing silica powders and gels [58–66]. Some scholars have used RHA to prepare mesoporous and zeolites silica [68–70]. The traditional technology to prepare silica aerogels was sol–gel polymerization of silicon alkoxides, and tetraethyl orthosilicate (TEOS) had been always the appropriate silicon alkoxide for the synthesis of silica aerogels [71–73] and at the same time played a role in strengthening the gel against forming cracks in preparation of silica aerogels. TEOS was non-toxic, but had a high production cost, so it was urgent to search for economic resource for preparing silica aerogel. RHA was the natural alternative as a cheap silica source [67, 74–76].

A method with low energy had been proposed to prepare pure silica from RHA and the extraction yield could be up to 91 % [63, 77]. Nonetheless, the resulting silica xerogel prepared through this method contained more than 4 % of sodium as pollutants, which need an extra washing step and a drying step to lower the concentration of sodium below 0.1 %. In order to make up for this disadvantage, Kalapathy [78] suggested an improved method for preparing silica xerogel by adding RHA into hydrochloric acid, oxalic acid, or citric acid solution at pH 4.0, and as a comparison, silica xerogel was prepared by the former method that was at pH 7.0. The results indicated that silica prepared by oxalic acid or citric acid at pH 4.0 contained less content of sodium and carbon than that prepared at pH 7.0. This modified method did not demand an additional washing step to prepare silica and there was little difference in the yield of silica no matter what kind of acid was used and no matter how the pH of silica precipitation was controlled.

Della [79] pointed out that RHA was an alternative source of high specific area silica. The RHA sample after burning out at 700 °C for 6 h presented the highest yield of silica powder, up to 95 %. After wet milling, the specific surface area of the particles was increased from 54 to 81 m^2/g. Patel [80] had found that the carbonization temperature had better <700 °C to avoid silica with amorphous form transforming crystalline form. It had been reported that reheating the ash in order to remove carbon residues required a higher temperature and quite a long time, and the consequent effect was that amorphous silica converted to crystalline form [8], but in this article, the structure of silica still remained in amorphous form after incinerating RHA at 700 °C for 6 h, which was adverse to the results reported by previous researchers.

Shen [81] discussed the effect of calcination parameters, containing the time and temperature on the silica prepared from original and water-leached RHA (ORHA and LRHA, respectively). The samples were obtained by varying the calcination time and temperature for original and water-leached RH (ORH and LRH, respectively). It was concluded that the silica in ORHA was susceptible to the calcination conditions, which was short calcination time and low calcination temperature led to amorphous silica forming. Nevertheless, in a wide range of calcination conditions, the silica in LRHA could still remain amorphousness, which confirmed the advantage of leaching on preparing silica with the amorphous form from the RH. Consequently, in order to prepare more active amorphous silica from the RH, the short calcination time and the low calcination temperature as well as the leaching procedure was essential.

An [82],one of our team members, developed a green route to prepare silica powders by using RHA as well as a waste gas. Na_2CO_3 was used as extraction reagent for silica, while CO_2 obtained from the waste gas after cleansing was used as a precipitating reagent. Under optimum extracting conditions, the silica yield could be up to 72.52 %, they were 60 min of carbonation time, 4 h of extraction time, 5:1 of impregnation ratio and 20 wt% of Na_2CO_3 concentration. The moisture and silica content of the resulting powders were 1.58 and 98.20 %, respectively. Furthermore, as the extraction reagent, Na_2CO_3 could be recycled in the silica extraction process, which lowered the cost of dealing with a large amount of industrial waste in traditional craft. Therefore, this alternative approach was a green and sustainable development process.

In our recent studies, sodium metasilicate was prepared from RHA by a green and low in production cost chemical route with various concentrations HCl and NaOH reaction at a series of temperatures and time. The present work of our team, extracted most of amorphous SiO_2 from RHA is one of the important experiment steps, and then discussing the effect of experiment parameters, containing reaction time, temperature, concentration of NaOH and the ratio of sodium hydroxide and A-RHA solid–liquid on the silica dissolution from original RHA. Silica was prepared from RHA by hydrochloric acid pretreatment in a water bath kettle whose aim was to remove impurity ions such as iron ion, ferrous ion, calcium ion, magnesium ion, and then subsequently filtering. And washing to neutral the residue was called A-RHA. Then, A-RHA reacted with different concentrations of NaOH solution in a water bath pot in order to dissolve silica.

The detail experimental data on the dissolution rate of silica are shown in Figs. 1, 2, 3, and 4. Figure 1 shows that silica dissolution rate with the increase of solid–liquid ratio increased significantly, when the maximum value of the dissolution rate of silica was sodium hydroxide and A-RHA solid/liquid ratio of 1:8, then silica dissolution rate decreased with the increase of solid–liquid ratio, which decreasing speed was slow. With the reaction time and the reaction temperature augmenting, the silica dissolution rate increased continuously, and it reached the maximum at 2.5 h and 90 °C (shown in Figs. 2, 3). From Fig. 4, we can see that the silica dissolution rate climbed and then declined with the increase of the mass fraction of NaOH aqueous solution. When using 10 wt% NaOH aqueous solution, the silica dissolution rate is the highest.

Tang [83] prepared silica aerogel from RHA by supercritical carbon dioxide drying. The results showed that the obtained silica aerogel from RHA was a light and white mesoporous solid material with a bulk density as low as 38.0 kg/m^3, porosity as high as 98.3 % and a specific surface area as high as 597.7 m^2/g. The pore diameters inside the aerogel averaged 10–60 nm. The two silica aerogels had similar pore volumes and densities, whereas the specific surface area of the aerogel from TEOS was higher than that from RHA and their color was entirely different. The former was transparent and the latter was white. Although ambient pressure could be used as the condition in the process of drying, the result was a xerogel instead of an aerogel. The reason was that cracking and shrinkage of the network of gel was caused by capillary pressure during drying of the gel under ambient pressure, which resulted in the xerogel being generated with very low pore volume and specific surface area as well as high density. The capillary pressure gave rise to the shrinkage of a gel, which could be controlled by reducing the surface tension of

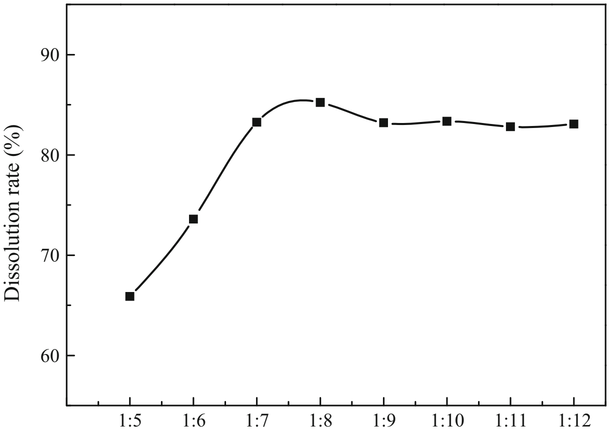

Fig. 1 The dissolution rate of SiO_2 at different sodium hydroxide and A-RHA solid/liquid ratios

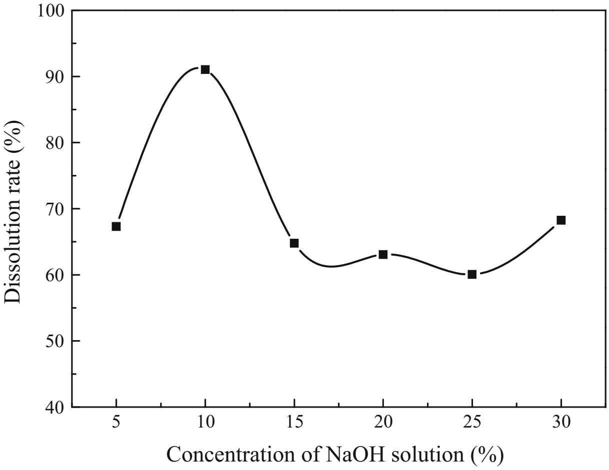

Fig. 2 The dissolution rate of SiO_2 at different concentrations of NaOH solution

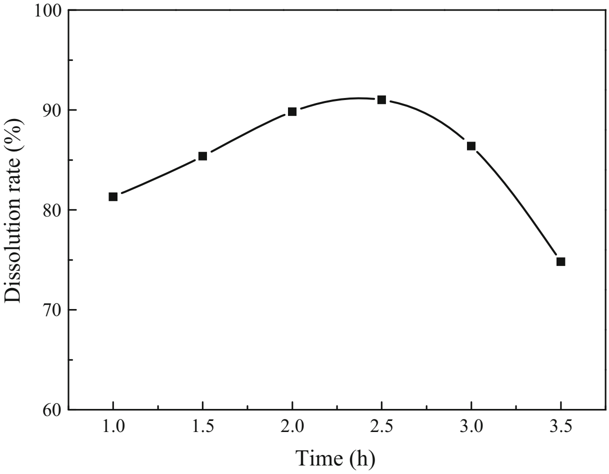

Fig. 3 The dissolution rate of SiO_2 at different reaction times

the pore liquid [84, 85]. Moreover, the supercritical drying was the best option to eliminate surface tension to prepare the silica aerogel and at the same time keeping the gel structure from breaking. From this paper, we might get a revelation that though the aerogel from RHA was not as good as that from TEOS, RHA was still utilized as a fitting precursor to prepare silica aerogel.

Tadjarodi [86] prepared nano-porous silica aerogel from RHA by drying at atmospheric pressure. Two kinds of RHA were obtained: mild-slope and quick-slope. The results revealed that the sample of RHA obtained from quick-slope possessed lower “limit of identification” and more silicon and could be used as the

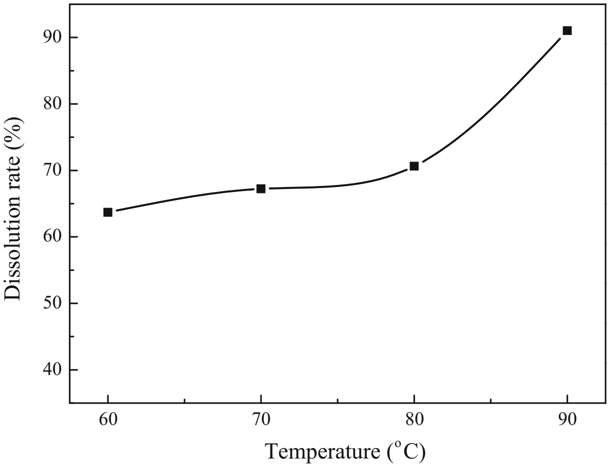

Fig. 4 The dissolution rate of SiO_2 at different reaction temperatures

material to prepare silica aerogel. Two kinds of silica aerogel were obtained: TEOS-doped silica aerogel and silica aerogel without TEOS doped. To a large extent, the pore structure of silica relied on the blended TEOS under atmospheric pressure drying. In the TEOS-doped silica aerogel, the average pore size porosity, the pore volume, and the specific surface area were increased. On the contrary, its density was reduced, whereas the silica aerogel without TEOS-doped acquired lower average pore size, lower pore volume, lower specific surface area, lower porosity and higher density. The obtained silica aerogel with TEOS doped was a lightweight and mesoporous solid material with the average pore size 9.8 nm, the pore volume 0.78 cm^3/g, the specific surface area of 315 m^2/g, the bulk density 0.32 g/cm^3, and the porosity 85 %. From the above two papers, we might be able to summarize that RHA could be used to replace a part, but not all of TEOS to prepared silica aerogel.

RHA as an adsorbent

Environmental pollution is one of the most serious ecological problems at present; that is, the rapid development of industrialization has led to a large amount of various heavy metals and dyes, which are poisonous both to humans and to other creatures, entering the environment. Today, the primary objective is to develop an appropriate technology and to take a suitable method in order to protect the pollution from hazards, namely reduce the hazards to a much lower level. Different physico-chemical processes are used to treat these wastewaters with great success, such as ion exchange [96], membrane separation [95], adsorption [92–94], reverse osmosis [91], fertilization [90], electrochemical precipitation [89], solvent extraction [88], and electro dialysis [87]. Among these techniques, adsorption is considered a friendly technology for the cleanup of wastewater [97].

Activated carbon (AC) is one of the most popular adsorbents, which has shown considerable success and has been used widely because of its high capacity for adsorption. However, particularly in developing countries, the application of commercial AC as an adsorbent is limited due to its high cost and 10–15 % loss during regeneration. Therefore, several researchers have sought a feasible method of using much cheaper materials to purify wastewater from various dyes and other pollutants [98–105].

RHA, which mainly contains two elements: Si and C, with large specific surface area and high degree of porosity, has good adsorptive properties and can be an effective alternative for AC. Previously RHA had been successfully used as an effective absorbent for removing biodegradable, toxic, and other contaminant from effluent [106–110].

The adsorption of heavy metals on RHA

Naiya et al. [111] treated the adsorption of lead (Pb(II)) on RHA from aqueous water. The maximum removal efficiency for Pb(II) adsorption could reach 99.3 % at optimum conditions, which were found to be an equilibrium time 1 h, adsorbent dosage of 5 g/l of solution, and pH of 5.0. The results also revealed the adsorption was a natural chemical process. The practical application was to use RHA into wastewater containing Pb(II) from a battery factory. The removal efficient was found to be 96.83 ± 0.3 %, and the final concentration conformed with the norms for waster water discharge.

Feng [112] attempted to use RHA, an agricultural waste, as an adsorbent to remove mercury (Hg(II)) and Pb(II) from aqueous solution. It was found that RHA was a suitable adsorbent for the adsorption of Hg(II) and Pb(II) ions, and the adsorption rate and adsorption capability for Hg(II) ions were much slower and lower than that for Pb(II) ions. The lower concentration of potassium nitrate supporting the electrolyte solution the higher the pH of the solution and the finer the particles of RHA were used, the greater the amount of Hg(II) and Pb(II) that were removed by RHA.

Totlani [113] developed an adsorbent by means of chemically modifying RHA, called carbon-embedded silica (CES), and then carried out the adsorption of nickel (Ni(II)) on CES and RHA, respectively, as the comparison. The results indicated that CES, with a larger specific surface area and more porous structure, consequently had a much higher adsorption capacity than the parent compound. For the CES sample, the optimum dosage for the adsorption of Ni(II) ion was up to 0.3 g/50 ml of the Ni(II) ion solution, and adsorption capacity came out to be 91 mg/g, whereas, for the RHA sample, the optimum dosage for the adsorption of Ni(II) ion was 0.6 g/50 ml of the Ni(II) ion solution and the value of adsorption capacity was as low as 5 mg/g. Thermodynamic analysis showed that the adsorption was an intensively endothermic process that was a spontaneous reaction, especially at higher temperatures. The negative values of ΔG still indicated that this reaction was spontaneous. Furthermore, there was a more valuable application that was spent CES containing Ni could be served for a catalyst [114]. Table 2 lists previous

Table 2 Previous research in the utilization of activated RHA as novel adsorbents for different applications

Adsorbate	Sorbent material	C_0 (mg/l)	Adsorption capacity (mg/g) or removal percentage (%)	Applicable isotherm models	References
Pb(II)	RHA	39.74	96.83 ± 0.3 %	Freundlich, Langmuir, and Dubinin–Radushkevich	[173]
Cd(II)	RHA	39.87	97 ± 0.6 %	Freundlich, Langmuir, and Dubinin–Radushkevich	[173]
Zn(II)	RHA	39.17	96 ± 0.8 %	Freundlich, Langmuir, and Dubinin–Radushkevich	[173]
Cu(II)	RHA	40.82	95 ± 0.9 %	Freundlich, Langmuir, and Dubinin–Radushkevich	[173]
Hg(II)	RHA	40	–	Langmuir and Freundlich	[112]
Ni(II)	CES	20	91 mg/g	Langmuir and Freundlich	[113]
Ni(II)	RHA	20	5 mg/g	Langmuir and Freundlich	[113]
Methylene blue	RHAC	60	9.83 mg/g	Langmuir and Freundlich	[173]

research in the utilization of RHA AC as adsorbents for different applications [112, 113, 173].

Srivastava [115] removed zinc (Zn(II)) and cadmium (Cd(II)) metal ions by RHA from binary aqueous water. The study showed that maximum adsorption for both Zn(II) and Cd(II) metal ions occurred at pH_0 6.0, and at lower initial concentration of adsorbate in the solution prompted a larger proportion of metal ion removal. Optimum dosage (m_{opt}) was found to be 10 g/l, and researchers had suggested that using different adsorbents caused different values of m_{opt} for the adsorption of Zn(II) and Cd(II) ions. Under similar experimental conditions, the RHA for Cd(II) possessed less affinity than that for Zn(II) in either single component or the binary aqueous water, which was similar to other investigators [116]. It was also declared that the interaction effects of Zn(II) and Cd(II) ions on the sorption of Cd(II) ions by using RHA was considered to be adverse. It might be said that the RHA could be used as an appropriate adsorbent to individually or simultaneously remove of Zn(II) and Cd(II) ions from wastewaters containing metals. Moreover, it was necessary for the disposal or regeneration of the exhausted adsorbent, several solvents had been used for the desorption experiments. Consequently, any of the inorganic acids could be seemed as the perfect eluent for the study of the system, but it was not important of the desorption efficiency. Some reporters had proposed that the adsorption of trace metals was an incompletely reversible process [117–122]. In the current studies, it seemed that the sorption of metal ions on RHA hindered the desorption of metal ions from the exhausted RHA. With a heat value of 9.68 MJ/kg [106], RHA could be utilized to make blended fuel briquettes. The bottom ash after combusting could be added into the concrete mixtures [123].

In two separate papers [106, 110], Vimal Chandra Srivastava described the effect of individually removing Zn(II), Ni(II), and Cd(II) metal ions from aqueous waters by RHA as an adsorbent. The maximum adsorption for metal ions occurred at adsorbent dose ≈ 10 kg/m^3 of solution, pH$_0$ ≈ 6.5, and the equilibrium time ≈ 5 h. However, these experiments were normally carried out in such a way to select optimize conditions, that was "one factor at a time" which overlooked the interaction effects among multiple factors on the procedure of adsorption. In order to make up for the inadequacy of this methodology, Srivastava [124] put forward a proposal to use Taguchi's experimental design methodology, and at the same time, he firstly studied the simultaneous adsorption of Zn(II), Ni(II), and Cd(II) ions on RHA and quantified the interactive effect of one metal on the sorption of the other due to that industrial effluents generally contained several metals. Taguchi's orthogonal array, which had been applied by several chemical and environmental engineers [125–131], was recently a greatly efficient method for studying the efficiency of various factors and potential interactive effects between multiple factors at a time [132]. The results showed that this new method needed fewer experiments, and the optimum adsorption of Zn(II), Ni(II), and Cd(II) ions on RHA occurred at $C_{0,i} = 0$–100 mg/l, pH$_0 = 6$, $T = 40$ °C, $m = 10$ g/l and $t = 60$ min. The study showed that RHA was a feasible replacement of the AC for the effective sorption of metal ions from aqueous waters and the Taguchi's method was equal to improve the experiments for the perfect sorption of entire metal ions.

The adsorption of oil on RHA

Vlaev [133] used RHA to clean water that was polluted by diesel fuel or crude oil. Two samples of RHA produced under controlling combustion condition of the RHs in inert (nitrogen) or air atmosphere, respectively, were black rice husk ash (BRHA) and white rice husk ash (WRHA), which had porous and amorphous structure as well as high specific surface area [134–136], and was possibly seemed as adsorbents, concrete, cement, rubbers, and filler of polymers or for other applications [137–140]. It could be concluded by comparing the adsorption of water, WRHA was higher than that of BRHA, since WRHA was more hydrophilic; but the adsorption of crude oil, diesel fuel, and hydrocarbons, WRHA was less than BRHA, and the sorptive effect of BRHA was higher for crude oil than for diesel. Based on this tendency, it could be concluded that BRHA was a more appropriate adsorbent for cleansing crude oil and multiple hydrocarbons bilge water or in water basins. Moreover, the exhausted BRHA with multiple hydrocarbons, diesel fuel, and crude oil possessed higher heating value so that it could be reburnt in steam generators, industrial ovens, or incinerators. In such a manner, two effects were attained, not only economical, but also ecological.

The adsorption of SO_2 on RHA

Lee [1] researched the optimum conditions for preparing a flue gas desulfurization absorbent by using RHA. The center of the experimental design was carried out to simultaneously test the effect of the amount of calcium sulfate ($CaSO_4$), amount of RHA, hydration period, and hydration temperature on the specific surface area of the resulting absorbent. The results indicated that the lower value of four experimental variables in favor of the formation of absorbent with higher surface area. What was more, the aim of adding $CaSO_4$ into the parent compound was to ensure the feasibility of reusing the exhausted absorbent. It was furthermore said $CaSO_4$ was added into the parent compound could be very conducive to the hydrated products formed in the process of preparing absorbent by using coal fly ash (CFA) [141, 142]. However, this phenomenon was diametrically opposite for absorbent prepared from RHA. This distinction was most probably caused by the different amount of silica in RHA and CFA. Due to the high amount of silica in RHA, it was no longer essential for the role of $CaSO_4$ for keeping the reactivity of the CaO or $Ca(OH)_2$ to RHA (silica). On the contrary, the existence of $CaSO_4$ covered the surface of CaO or $Ca(OH)_2$ and thus decreased its reactivity to RHA (silica). Therefore, the content of $CaSO_4$ added into the preparation mixture should not be too much, and preparing an absorbent from RHA was more inexpensive than the traditional CFA.

The adsorption of other substances on RHA

Lakshmi [143] and Mane [144] evaluated the adsorptive capacity for Brilliant Green (BG) dye and Indigo Carmine (IC) dye from aqueous water by RHA, respectively. The studies showed that RHA could be an economic and effective adsorbent for the adsorption of IC dye and BG dye from aqueous water.

Proctor and Palaniappan [145, 146] had reported the sorption of free fatty acid from soy oil on RHA. Adam [147, 148] had reported that the ability of RHA to adsorb saturated fatty acid followed a Langmuir isotherm and the free energy of sorption for saturated fatty acid on RHA pretreated by acid was approximately −28 kJ/mol. RHA without pretreating could adsorb free fatty acids from palm oil. Furthermore, it was easy to extract the fatty acids that were adsorbed on RHA by acetone [149]. Adam [150] also suggested that RHA was regarded as an effect adsorbent of palmitic acid.

Lataye [151] had studied the sorption of pyridine (Py) from synthetic aqueous waters on RHA that had a higher adsorption rate as well as a better affinity for Py and spent a shorter equilibrium adsorption time. Moreover, the exhausted RHA could be easily filtered, dried, and then used in an incinerator or boiler furnaces. Therefore, its heat value was able to recycle.

Synthesis of AC and SiO_2 at the same time

RHA was a large number of agricultural waste and the main components were silica and carbon. Therefore, RHA had a wide range of applications as building materials in concrete [152, 153] or as an adsorbent [154–163] and the silica source [164–169] and, which could also be sufficiently proven by the above content of the present article. However, there were only a few references on preparing silica and AC with a consecutive method.

An [170] researched the preparation of AC and silica powders from RHA at the same time. Firstly, the RHA was leached by acid to eliminate the metal impurities, and then was boiled with alkali to dissolve the silica. The filter residue was to synthesize AC and the filtrate was to prepare silica powders. The leaching yield of silica from RHA was 84.57 %. The resulting silica powders were hydrated with high purity and a relatively smooth surface, moreover, with amorphous structure. The solid residue was activated with potassium hydroxide (KOH) to prepared AC which possessed mix pore structures of micropore and mesopore, and its iodine number could reach 1259.06 mg/g. In brief, silica powders and AC could be prepared from RHA at the same time.

Our laboratory group researched a sustainable route for preparing silica and AC simultaneously from RHA [172]. Figure 5 shows that the detail experimental procedure mainly included three steps: (a) activation stage: RHA was activated with Na_2CO_3 powder, and CO_2 released from this process could be reused to precipitate silica; (b) Dissolved stage: the RHA after activation was continuously boiling for some time with a large amount of water and then filtered. The AC was prepared by thoroughly washing solid residue to neutral with distilled water and then dried; (c) Carbonization stage: the filtrate was neutralized by CO_2 and then precipitated to separate SiO_2. In the whole synthetic procedure, Na_2CO_3 powders could be recycled and reused as the reactant to activate RHA, which stated that inexpensive, sustainable, and being environmentally friendly were the dominant features for this method. The particle size of silica was approximately 40–50 nm and the leaching rate was about 72–98 %. The capacitance value, iodine adsorption capacity, and surface area of AC could achieve 180 F/g, 1708 mg/g, 570 m^2/g, respectively.

In a separate paper, Yan Liu, who was a member of our team, selected K_2CO_3 instead of Na_2CO_3 as the activation agent [172]. The average pore size and the surface area of the AC were 4 nm and 1713 m^2/g. The capacitance value was up to 190 F/g and the maximum adsorption capacity of methylene blue for AC reached 210 mg/g. The particle size of silica was 40–50 nm and the leaching rate could be up to 96.84 %; and K_2CO_3 could be recycled. In order to compare the effect of both activation agents (K_2CO_3 and Na_2CO_3), Table 2 detailed description the optimum conditions of pyrolysis process and the performance of produce. From Table 3 we

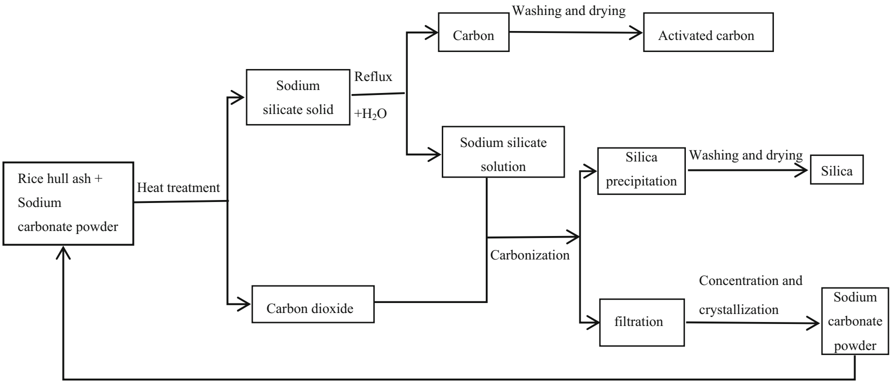

Fig. 5 The synthetic procedure for the preparation of AC and silica simultaneously from RHA

Table 3 The optimum conditions of pyrolysis process and the performance of produce using different activation agents (K_2CO_3 and Na_2CO_3)

Activation agent	K_2CO_3	Na_2CO_3
Activated temperature (°C)	1000	900
Activated time (min)	90	45
Impregnation ratio	1:5	1:1.75
Volume of water (ml)	120	350
Extraction rate of silica (%)	96.84	93.79
The average diameter of the silica (nm)	40–50	40–50
The maximum adsorption for iodine (mg/g)	–	1708
The maximum adsorption for methylene blue (mg/g)	210	–
Capacitance value of AC (F/g)	190	180
The recovery rate of activation agent (%)	94.2	92.3
References	[172]	[171]

could conclude, as the activation agent, K_2CO_3 was so lighter dosage and developed the hole structure, prodigious surface area as well as the adsorption capability for the obtained AC that K_2CO_3 owned more superiority than Na_2CO_3.

Due to containing a large quantity of amorphous silicon dioxide and being prepared by a simple synthetic method, RHA is widely considered as an organic, environmentally friendly, and recyclable material. For example, aluminium and iron hydroxides were modified by RHA to remove fluoride and arsenic from drinking water [174]. A good overview of RHA preparation from rice husk and application is given by Fig. 6. In a future study, RHA with nanoscale microstructure, fine and homogeneous pore size can be produced to effective application of nanomaterials in adsorbent and catalyst. On the other hand, it is a prospective evolution research orientation that RHA is synthesized to thermal insulation and building material, because of possessing the performance of small thermal conductivity.

Conclusions

RHA is a kind of agricultural waste and it is also available abundantly obtained from the combustion of RH at a throw-away price. With the progress of science and technology, the employment of RHA will have been unceasingly researched, the technique will have come to mature and the products will have been involved in various aspects of social life. Thus, it is certain to deserve a good economic return, making full use of the advantage of rice production in our country (China), actively expanding application areas and promoting the development of relevant industries. Based on setting forth the comprehensive utilization of highly active RHA, this review displays the broad prospects of the development of RHA.

It is considered that the most promising areas of RHA are as pozzolanic material and as an adsorbent. After combustion, the presence of plenty of amorphous SiO_2

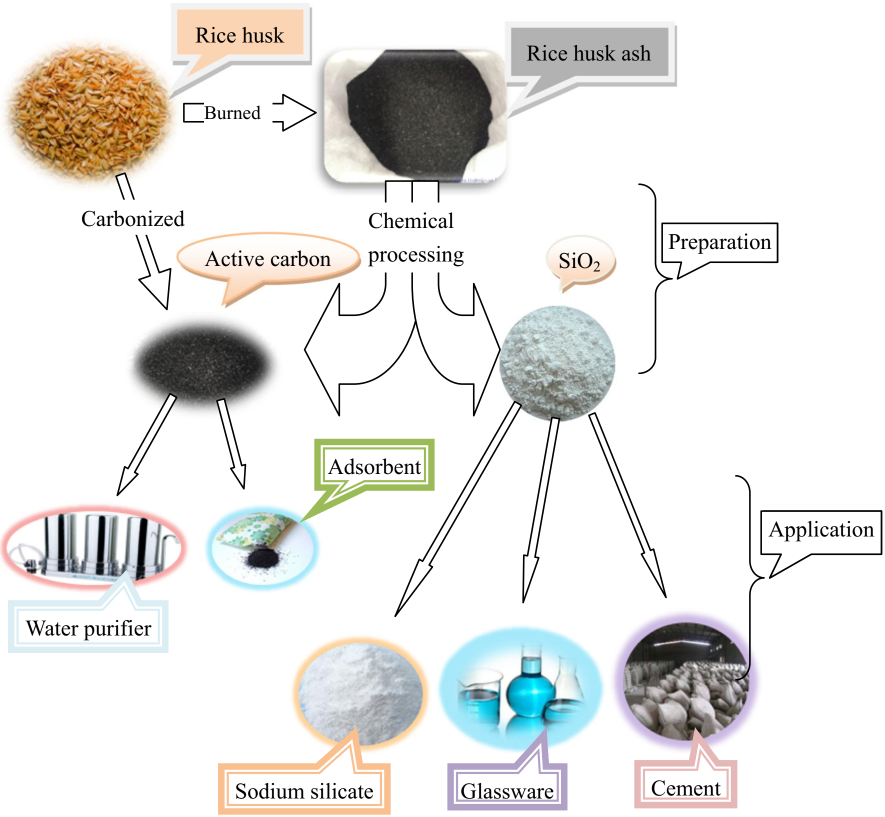

Fig. 6 The scheme of RHA preparation from rice husk and application

endows RHA with perfect pozzolanic activity. It is beneficial to the development of concrete in the direction of higher strength as well as better performance and reduces the cost of manufacture. What is more, SiO_2 and C in the RHA both own adsorption capacity. The adsorbent that was produced by RHA as the raw material possesses several time values beyond RHA's own value. But the performance of RHA was very sensitive to combustion conditions on RH, it is imperative to study on how to obtain ideal performance and stable quality of RHA. If breaking down a barrier of controlling temperature and realizing the large-scale industrial production, it will open up a new path for the application of the RHA.

In summary, RHA is an environmentally friendly power with low-energy, high-efficient, green and potential economic benefits, social benefits and environmental benefits. Various advantages of RHA have a positive effort on providing new momentum for local or more regional sustainable development in the future.

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