Rev Environ Sci Biotechnol (2016) 15:47–65
DOI 10.1007/s11157-015-9388-0

REVIEW PAPER

Recovery of value added products from rice husk ash to explore an economic way for recycle and reuse of agricultural waste

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Abstract Rice husk ash (RHA) is the major by-product left after the burning of rice husk, which is profusely present throughout the process of the rice milling. The burnt rice husk, as RHA, in turn causes more environmental pollution and its disposal becomes a difficult problem, hence requiring serious attention from the scientific community regarding its disposal and proper reuse if possible. The major economic reason for recycling the ash is the value added products which can be generated from it. The focus is on the use of RHA as adsorbent and subsequent silica production owing to the fact that the ash is mainly composed of carbon and silica. As regards other potential applications of ash, research is still going on and some of the products, which are under development phase, have also been brought to limelight in this review. This literature review provides an effective scheme to utilize RHA and discussed process pathway for economically valuable products to provide a solution to the problem associated with its proper disposal through superior recycle of this agriculture waste.

Keywords Rice husk ash · Silica · Adsorbent · Catalyst · Agricultural waste

1 Introduction

Rice is the principal source of food for billions of people worldwide, and its cultivation covers about 1 % of the earth's surface, with the yearly global production around 600 million tonnes presently. According to the statistical data of FAO, in the year 2010, rice production was approximately 697.9 million tonnes (Rice Market Monitor 2010). For every 100 kg of rice produced, 22 kg of rice husk is generated, making rice husk and rice husk ash abundantly available in rice producing areas (Rice husk ash 2011). Raw rice husk typically composed of 35 % cellulose, 25 % hemicellulose, 20 % lignin, 17 % ash (a total of 94 % silica) and 3 % moisture by weight (Chaudhary et al. 2002).

A considerable part of this waste is used for cattle feed but mostly it is dumped off as waste for landfill, bedding material for animals, or otherwise burnt to generate power for the rice mills which produces rice

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husk ash (RHA) as by product (Ayswarya et al. 2012). Due to the presence of very hard surface, high silica content and small bulk density, rice husk residues become a dangerous source of pollution (Zhang et al. 2015). Depending upon the method and incineration conditions, typically two types of ash are produced i.e. white rice husk ash (WRHA) and black rice husk ash (BRHA) (Tavlieva et al. 2013). RHA contains 55–97 % silica by weight, depending on the geography where the rice is grown, which is either in amorphous state or crystalline state (Ayswarya et al. 2012). In spite of silica being the predominant component in RHA, trace amounts of other elements such as potassium, magnesium, calcium and sodium are also present (Kalapathy et al. 2000). This RHA is mostly dumped in the open environment, which causes severe water and land pollution and subsequent health related problems. Water pollution and its unavailability for the generations to come, are given the same importance as global climate change in this twenty-first century (Shi et al. 2010). Thus, presently, this issue has been garnering enough attention with regard to its proper disposal and innovative ways of utilization of what otherwise would have been considered as an agricultural waste.

In the last decade, a large number of studies had addressed the issues of using the rice husk biomass into useful commercially valuable products (Zhang et al. 2015). The concern for environmental pollution and conservation of resources have inspired the use of RHA as catalyst carriers, fillers in cement, fertilizers and production of pure silica, silica gels, geopolymers, sand filled polymers (Soltani et al. 2015). Studies showed that available RHA from rice mills can be effectively used as an adsorbent for the treatment of wastewater generated from various sources like iron and steel plant, dye industries and even the rice mill itself (Kumar et al. 2015). With the surge in global activated carbon price, a search for an alternative to commercial activated carbon is of utmost importance (Roskill 2009). A major utilization of RHA which has been explored is the generation of silica and subsequent catalysts preparation from it (Adam et al. 2012). Silica is a valuable material having high commercial value due to its demand for making semiconductor and glass. Silica in spite of being the most abundant oxide in the earth's crust, yet it is made predominantly by synthetic processes for its use in technological applications. Thus the use of RHA to generate silica is worth mentioning (Kumar et al. 2015). Preparation of silica from RHA involves different techniques and these have been studied extensively in different researches (Chang et al. 2006; Chen et al. 2010; Kumar et al. 2015).

Keeping in mind the aforementioned scenario with regards to RHA utilization, the present bibliographical review strides to elucidate a preliminary base for the origin, properties and potential prospects of judicial RHA utilization and the future prospects in reference to value added products from this agricultural waste. This literary work has been prepared to contribute in the analysis of past and present research works carried out so far in the field of processing RHA to derive values from it. This review aims in generating an up to date scenario of the status of RHA as a potential replacement for expensive commercial activated carbon and production of valuable silica from RHA. The aim of this literature review is to familiarize the readers with the knowledge of RHA and provide a proper scheme for economic utilization of RHA giving details of processes for the preparation of different value added products.

2 Characterization and composition of RHA

Although the composition of rice husk varies with different sample based on diverse geographic and geological conditions, the analysis of the typical rice husk from any rice mill reveals that it usually contains mostly organic compounds (94.99 % by weight) and a little amount of inorganic compounds. The organic composition of rice husk is given in Table 1 (Sharma et al. 1984). The difference in composition may be attributed to the variety of paddy, the climatic

Table 1 The organic composition of typical rice husk collected from rice mill (Sharma et al. 1984)

Organic constituents	Weight percentage
α-Cellulose	43.30
Lignin	22.00
D-Xylose	17.52
L-Arabinose	6.53
Methylglucuronic acid	3.27
D-Galactose	2.37
Total	94.99

condition in which it grows, fertilizer used, geography and soil in which it grows (Chaudhary and Jollands 2004). Since 1938, it was known that rice husk contains silica (Martin 1938), the chemical composition of rice husk has been analyzed and one such analysis (Rao et al. 1989) is given in Table 2. The chemical composition for rice husk from Jorhat, India and USA is provided in the analysis. The silica present in rice husk is in hydrated amorphous form, either opal or silica gel (Mitchell et al. 2004).

Rice husk has scantly been utilized despite possessing such valuable chemical composition. It is usually burned due to its high calorific value to generate power to run the rice mill. Rice husk when used for electricity generation instead of fossil fuel reduces greenhouse effect by releasing CO_2 trapped plant and hence maintaining a zero CO_2 addition in the atmosphere by using biomass over the entire life cycle (Soltani et al. 2015). Rice husk, an easily available biomass source having low moisture content (8–10 %) and decent calorific value ranging between 12.1 and 15.2 MJ/kg (Beagle 2006). The burnt off rice husk produces ash which is very rich in silica. Typically RHA contains more than 90 % silica, which is usually available in crystalline form (burnt at temperature 800–1200 °C). Under controlled burning at lower temperatures (around 500–600 °C), it forms highly reactive amorphous silica due to its fine size and large surface area (Le et al. 2015). The chemical composition of RHA has been tabulated in Table 3. A possible bonding between the silicon and the four monosaccharide molecules has been suggested by Patel et al. (1987) and shown in Fig. 1. The variation in composition is due to the different sources from which rice husk has been collected. In spite of differences in composition, the basic chemical components of RHA are Si, MnO_2, Al_2O_3, Fe_2O_3, K_2O, Na_2O, CaO and MgO (Liu et al. 2011).

Table 2 Chemical composition of rice husk (Rao et al. 1989)

Chemical component	Weight percentage in ash form	
	Jorhat, India	USA
Si as SiO_2	94.5	94.5
Ca as CaO	0.48	0.25
Mg as MgO	0.23	0.23
Al trace	0.21	1.30
Fe trace	0.62	0.54
Mn	0.11	1.09
K as K_2O	Trace	1.1
Na as Na_2O	Trace	0.78
P as P_2O_5	Trace	0.53
S as SO_4	Trace	1.13

For the purpose of morphological study of RHA, SEM images play a crucial role which indicate surface structures and porosity of the sample. It also shows fine particle size of RHA which is in the order of millimeter or lesser and pores of different sizes within the particle are also revealed by the images (Totlani et al. 2012). Images suggest that RHA has surface which is highly irregular and porous in nature (Naiya et al. 2009). Prior to SEM photographs, samples are usually spluttered with gold (Naiya et al. 2009). Figure 2a–d represents the SEM images of RHA obtained from different sources (An et al. 2011; Daud and Hameed 2010; Srivastava et al. 2006; Totlani et al. 2012). The fibrous species present among the fragments in the residues is most likely to be cellulose which is probably degraded and crystalline in its nature (Rosa et al. 2012). The size of the particles is seen to decrease as the time allowed for activation increases (Chen et al. 2011). Chemical structure of an adsorbent is important for the understanding the adsorption process. Fourier infrared transform (FTIR) study is an important tool which gives the idea about the functional groups present in the adsorbent and plays a vital role in adsorption of contaminants (Totlani et al. 2012). The FTIR plots of RHA before and after adsorption of contaminants are given in Fig. 3a, b where RHA has been used for the treatment of heavy metal ions (Srivastava et al. 2006), indigo carmine dye (Lakshmi et al. 2009). An adsorption peak in the range 3133–3568 cm^{-1} represents bonded hydroxyl groups which is present in the RHA (Chatterjee et al. 2012). Peaks around $\sim$2923 cm^{-1} may be due to the C–H stretching of aliphatic carbons or due to CH_2 or CH_3 deformation (Akhtar et al. 2010). The increased adsorption potential may be attributed to these stretching. Bands near 1630 cm^{-1} indicates the presence of nitrogenous groups present in the RHA and the band is due to the stretching of N–H bonds. Peaks around 1090 cm^{-1} are due to C–O stretching and this indicates presence of ester or phenol groups in the ash. Peaks around 1590 cm^{-1} indicates the presence if aromatics (Sharma and Uma 2010). Typical RHA shows the presence of these functional groups which is evident from the FTIR graphs presented in Fig. 3a, b.

Table 3 Composition of rice husk ash from various sources

Composition	Van et al. (2014)	Gastaldini et al. (2010)	Bhagiyalakshmi et al. (2009)	An et al. (2011)	Daifullah et al. (2003)	Mutuk and Mesci (2014)	Yeletsky et al. (2009)	Kumar and Gupta (2015)	Abo-El-Enein et al. (2009)
Al_2O_3	0.4	0.28	0.13	0.606	–	0.72	0.11	1.4	0.63
CaO	0.9	0.45	1.23	0.592	0.25	0.75	1.06	2.4	1.96
Fe_2O_3	0.3	0.14	0.07	0.423	<0.5	0.5	0.12	0.6	0.51
K_2O	3.39	1.55	0.78	1.952	1.10	2.2	2.17	1.9	2.10
MgO	0.6	0.28	0.25	0.221	0.23	0.27	0.33	2.1	0.70
MnO	–	–	0.33	–	–	–	0.08	–	0.04
Na_2O	0.04	0.08	0.08	0.078	0.78	0.1	0.30	0.3	1.45
P_2O_5	–	–	0.15	–	0.53	–	–	–	0.06
SiO_2	87.4	90	93.20	66.12	94.5	91.2	95.79	91.3	87.5
SO_3	0.4	0.02	–	–	0.6	–	–		–
Others	–	–	1.9	0.25	–	–	0.04	–	4.5

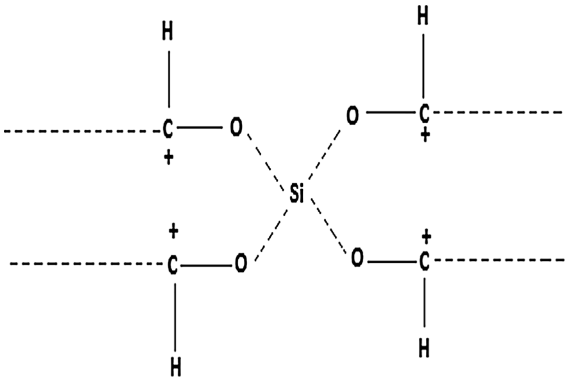

Fig. 1 Possible bonding of silicon with its adjacent monosaccharide in rice husk (Patel et al. 1987)

3 Utilization of RHA as an adsorbent

In the past few decades, the problems related to intense contamination of the soil, atmosphere and water has attracted many environmentalists all over the globe (Bhattacharya et al. 2006). A lot of resources have been associated with the eradication of contaminants and treatment of effluents before discharging them into the environment. In regards to liquid waste, several possible treatment techniques has been put to test, which includes coagulation, flocculation, sedimentation, floatation, membrane based processes, electrochemical processes, biodegradation, chemical oxidation, adsorption and ion exchange techniques. All these technologies have varying success with applicability and each one has challenged the other to become better and more superior technique in terms of cost, effectiveness and applicability (Foo and Hameed 2009a; Kumar et al. 2009). In regards to these treatment techniques, adsorption process have shown the maximum promise and turned out to be very efficient in many cases (Daifullah et al. 2004; Doke and Khan 2013). Thus, grew the importance of activated carbon for its adsorptive capacity with high surface area, porous structure, thermal stability, low reactivity towards acid and base (Jayaranjan et al. 2014) and its capacity to remove both organic and inorganic from aqueous medium, even from gaseous medium (Chingombe et al. 2005). The two main basic steps in preparing activated carbon for adsorption are the carbonization of the carbonaceous raw material and activation of the carbonized product. The activation can be achieved mainly by two possible ways—physical adsorption and chemical activation. In comparison to physical activation, chemical activation is more advantageous because of lower energy requirement for the carbonization process and formation of activated carbon of smaller pores (de Yuso et al. 2014). The major chemicals which are used as activating agents are $ZnCl_2$, H_3PO_4, H_2SO_4, K_2CO_3, KOH (de Yuso et al. 2014). Even though its prolific use as an adsorbent is inevitable, problems in regard to economy of the process and regeneration has been a major barrier in the success of activated carbon as the most prominent technique for effluent treatment (Foo

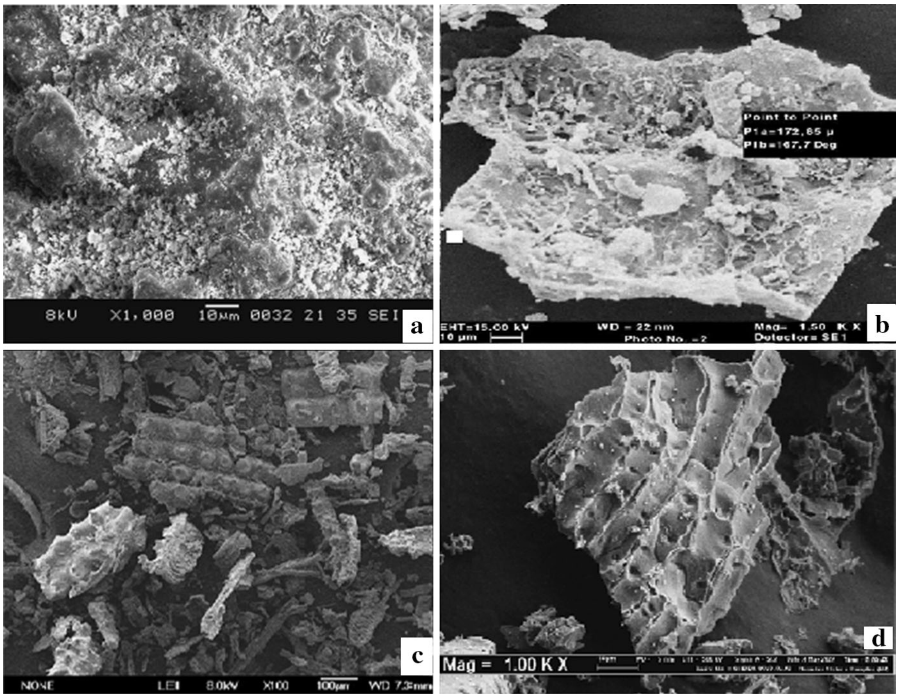

Fig. 2 SEM photographs of RHA from different sources (Totlani et al. 2012; Srivastava et al. 2006; An et al. 2011; Daud and Hameed 2010)

and Hameed 2009b). Owing to the high cost of activated carbon in the global market (Roskill 2009), efforts have been made by the researchers to generate activated carbon from low cost material like bamboo, tomato stems, orange peels, saw dust, sugar cane bagasse, maize, chitosan by chemical activation and heat treatment viz. carbonization (Dasgupta et al. 2015; Patel 2012; Song et al. 2015).

RHA, an agricultural waste is generated after burning rice husk in the boiler for power generation for rice mill. This makes RHA an abundantly available agricultural waste which otherwise has no use than being disposed off as landfill. Using RHA as an adsorbent has two fold advantages—firstly it provides a pathway to a successful yet economic solution to global water pollution problem through treatment of effluents by adsorption and secondly it gives a possible solution to pollution related issues arising from RHA disposals and prove RHA as a useful agricultural by-product, instead of labelling it as a waste (Foo and Hameed 2009c). Table 4 lists some of the previous works where RHA has been used as an adsorbent. It illustrates the adsorbate which has been adsorbed on to activated carbon prepared from RHA, the maximum adsorption reached and the condition at which it was achieved. The maximum possible adsorption is represented by either as a percent of total adsorbate adsorbed by the adsorbent or as the volume of adsorbate adsorbed per unit mass of adsorbent (q_e). One of the earliest attempt to use RHA as an adsorbent was by Tiwari et al. (1995), where Hg(II) was adsorbed on to RHA; a maximum of 98 % removal was achieved under the best suited condition of pH 6, and a contact time 180 min. Investigation made by Rocha et al. (2009) showed that for metallic ion adsorption by activated carbon followed the order Cd(II) > Cu(II) > Zn(II) > Hg(II) most of the time. Further modification of RHA was studied by Ganvir and Das (2011), where it was coated with aluminium to make it a better adsorbent for removal of fluoride from drinking water. The study shows a maximum fluoride removal of 10 mg/g was achieved by the process. Although RHA has been used for the adsorption of metals ions, phenolic compounds and gases, the major success was attained by using it for adsorption of dyes due of its extended surface area, high degree of surface reactivity and micro porous structure.

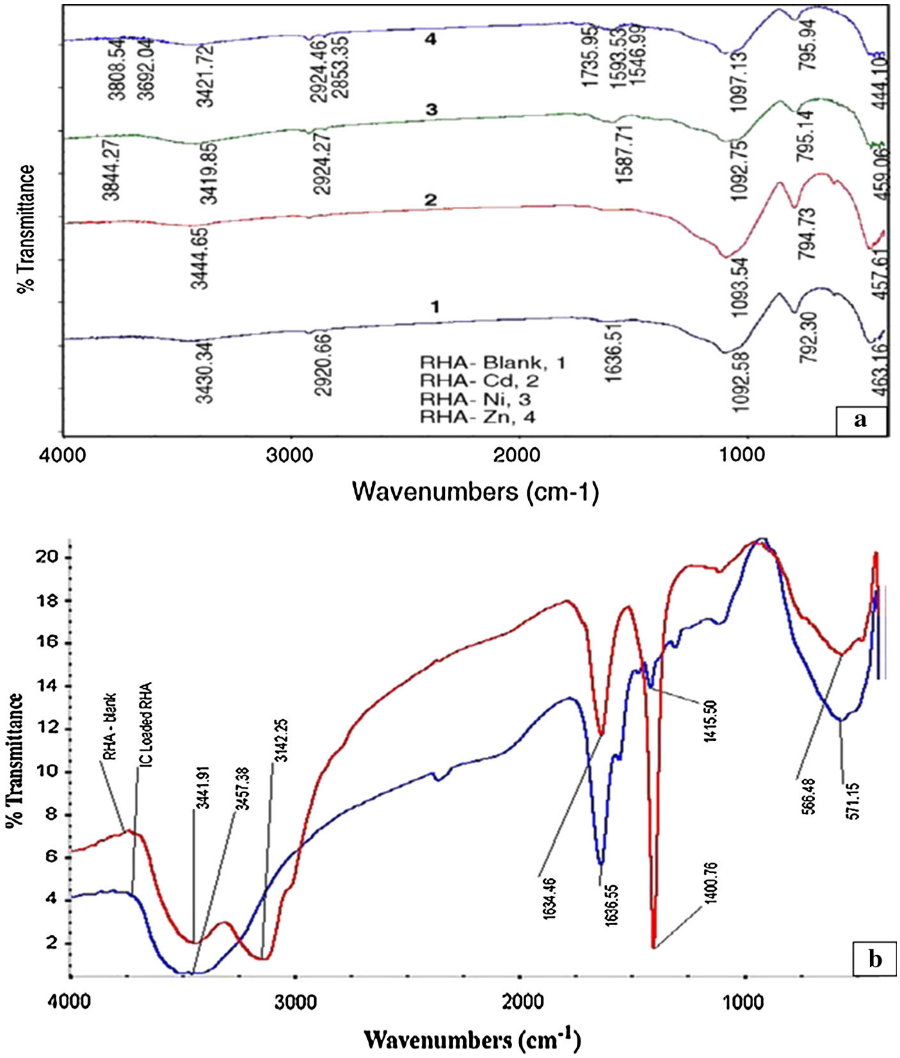

Fig. 3 FTIR plots of treated and untreated RHA, when RHA was used for the removal of **a** metal ions and **b** indigo carmine dye (Srivastava et al. 2006; Lakshmi et al. 2009)

Studying the adsorption requires kinetic and equilibrium analysis of the process. Kinetic and equilibrium study is important for the design and scale up of reactors, which is the very first step towards making the treatment process commercially viable (Chatterjee et al. 2012). Tables 5 and 6 represent the adsorption kinetics and the isotherms respectively. In most of the cases, adsorption onto RHA is well represented by Langmuir and Freundlich isotherms and the adsorption usually follows pseudo second order kinetics. The pseudo second order kinetics is represented by the following equation (Dasgupta et al. 2015). The kinetics is represented in terms of q (the amount of contaminant adsorbed per unit mass of adsorbent) where q_e is in the equilibrium condition while q_t is during any time instant.

$$\frac{dq_t}{dt} = k_s(q_e - q_t)^2 \tag{1}$$

where k_s is the pseudo-second order adsorption rate constant (unit: g/mg min). Equation (1) upon integration with boundary condition $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$,

$$\frac{1}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t \tag{2}$$

The initial adsorption rate, h (mg/g min) can be defined at t → 0 as

Table 4 Maximum adsorption achieved by rice husk ash when used as an adsorbent for adsorption of adsorbate under stated conditions

Adsorbate	Maximum adsorption	pH	Contact time	Reference
Cd(II)	29.85 %	6	5 h	Srivastava et al. (2006)
Copper ion	16.1 mg/g	6.01	2 h	Nakbanpote et al. (2007)
Brilliant green	85.56 mg/g	7	1.5 h	Tavlieva et al. (2013)
Fluoride	9–10 mg/g	7 ± 0.2	1 h	Ganvir and Das (2011)
Lead ion	91.74 mg/g	5	1 h	Naiya et al. (2009)
Methylene blue	1455.6 mg/g	7	30 min	Sharma et al. (2010)
Phenol	75 %	7	4 h	Aghav et al. (2011)
Humic acids	2.7 mg/g	6	1 h	Imyim and Prapalimrungsi (2010)
Indigo carmine	65.9 mg/g	5.4	8 h	Lakshmi et al. (2009)
Pyridine	79.50 %	6.2	5 h	Lataye et al. (2008)

Table 5 Most appropriate adsorption kinetics and their kinetic constants for uptake of various adsorbate under different operating conditions

Adsorbate	Kinetic model	Kinetic constant		K_s (g/mg min)	Conditions temperature (K)	Initial concentrations (mg/L)	References
		$q_{e,cal}$ (mg/g)	h (mg/g min)				
Brilliant green	Pseudo-second-order	3.83	0.4020	0.0274	300	20	Tavlieva et al. (2013)
Fluoride	Pseudo-second-order	15.08	11.84	0.0521	300	20	Ganvir and Das (2011)
Indigo carmine	Pseudo-second-order	4.86	0.2111	0.0089	303	10	Lakshmi et al. (2009)
Cd(II)	Pseudo-second-order	1.68	0.4288	0.1511	303	50	Srivastava et al. (2006)
Crystal violet	Pseudo-second-order	9.71	2.13	0.0013	303	50	Chakraborty et al. (2011)
Zn(II)	Pseudo-second-order	3.18	1.65	0.1630	303	50	Srivastava et al. (2006)
NH_4Cl	Pseudo-second-order	41.98	2.37	0.0013	308	1000	Kizito et al. (2015)
Slurry solution	Pseudo-second-order	46.21	2.45	0.0011	308	1000	Kizito et al. (2015)
Ni(II)	Pseudo-second-order	2.43	1.13	0.1913	303	50	Srivastava et al. (2006)

$$h = k_s q_e^2 \quad (3)$$

In case of adsorption process, which involves solid and liquid phases, the transfer of solute from the liquid solution is mainly characterized by external mass transfer (boundary layer diffusion) or inter-particle diffusion or both. The adsorption takes place via the three consecutive steps—firstly, solute form the bulk diffuses through the liquid film, then it diffuses through the pore of the adsorbent into the interior of the adsorbent and finally it get adsorbed onto the adsorbent (Ahmaruzzaman 2010). Among all the above mentioned three steps, the third and the final

Table 6 Equilibrium isotherm which represents the adsorption onto rice husk ash

Adsorbate	Equilibrium	Equilibrium constant	Equilibrium time (min)	References
Indigo-carmine	Freundlich	$K_f = 2.47$ ((mg/g)/(mg/l)$^{1/n}$)	480	Lakshmi et al. (2009)
	Langmuir	$K_l = 0.0151$ mg^{-1}		
	Temkin	$K_T = 0.8877$ mg^{-1}		
Crystal violet	Freundlich	$K_f = 19.22$ ((mg/g)/(mg/l)$^{1/n}$)	90	Chakraborty et al. (2011)
	Langmuir	$K_l = 4.174$ l mg^{-1}		
Methylene blue	Freundlich	$K_f = 1.74e{-}15$	30	Sharma et al. (2010)
Humic acids	Langmuir	–	60	Imyim and Prapalimrungsi (2010)
ά-Picoline	Freundlich	$K_f = 1.649$	360	Lataye et al. (2009)
Pyridine	Langmuir	$K_l = 0.030$	300	Lataye et al. (2008)
	Langmuir	$K_l = 0.036$		
	Freundlich	$K_f = 0.036$		

step is in equilibrium which is rapid and neglected while determining the overall reaction kinetics. The adsorption kinetics is mainly pseudo first order or pseudo second order with the adsorption being pore diffusion controlled (Gupta et al. 2003). The adsorption onto rice husk ash usually follows Langmuir, Freundlich and Temkin isotherm. The Langmuir isotherm is given by Eq. (4)

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_l q_m} \tag{4}$$

where K_l is the Langmuir constant (unit: L/mg) and C_e is the equilibrium adsorbate concentration in the solution. Equations (5) and (6) represents the Freundlich and Temkin isotherm of the adsorption process.

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \tag{5}$$

$$q_e = B_T \ln K_T + B_T \ln C_e \tag{6}$$

where in Eq. (5) K_F is the Freundlich constant (unit: (mg/g) $(L/g)^{1/n-}$) and n is the heterogeneity factor. In Eq. (6) the K_T indicates Temkin adsorption potential (unit: L/g) and B_T is the Temkin constant.

Thermodynamic parameters such as enthalpy change (ΔH°), entropy change (ΔS°) and Gibbs free energy change (ΔG°) of various adsorption processes have been listed in Table 7. The thermodynamic parameters are evaluated at a particular temperature; usually within the range between 300 and 320 K because most of the adsorption takes place in this temperature range. There is also a decrease in feasibility of adsorption as temperature increases because there is an increase in the escape of adsorbent molecules from the surface of the adsorbent due to high kinetic energy at higher temperature (Table 7).

The thermodynamic parameters have been calculated using the following equations (Nandi et al. 2009).

$$\ln\left(\frac{q_e m}{C_e}\right) = \frac{\Delta S^\circ}{R} - \frac{\Delta H}{RT} \tag{7}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S \tag{8}$$

The negative value of the Gibbs free energy indicates the feasibility of the reactions. The positive values of entropy change and enthalpy change indicates the spontaneity of the adsorption process. The adsorption process in case of 2,4-dichlorophenol is neither spontaneous nor feasible because of positive value of Gibbs free energy (Ahmaruzzaman 2010). For such adsorption processes, energy in form of heat is needed to be supplied from outside.

The details of the characteristic of the adsorbent prepared from RHA have been tabulated in Table 8 in terms of their particle diameter, BET surface area and pore volume. Generally the BET surface area lies between 10 and 100 m^2/g, while the average pore diameter (d) is about 45 Å. The pore area consists of 20 % micropores (having pore diameter <20 Å), 78 % mesopores (pore diameter lying between 20 and 500 Å) and 2 % macropores (with average pore diameter more than 500 Å). The RHA samples usually has a pore volume in the range of 0.03–0.04 cm^3/g.

Table 7 Thermodynamic properties for adsorption of different pollutants onto rice husk ash

Adsorbate	Temperature (K)	$-\Delta G$ (kJ/mol)	ΔH (kJ/m)	ΔS (kJ/Kmol)	References
Ni(II)	303	−3.59	11.33	0.025	Totlani et al. (2012)
Lead(II)	303	−9.23	28.92	0.132	Naiya et al. (2009)
Rhodamine B	313	−25.24	27.41	0.167	Jain et al. (2007)
2,4-Dichlorophenol	–	−7.1 ± 0.09	−25 ± 1	−0.061 ± 4	Akhtar et al. (2006)
Indigo carmine	–	−26.91	7.78	107.4	Lakshmi et al. (2009)

Table 8 The characteristics of adsorbent made from rice husk ash in terms of their mean diameter, BET surface area and pore volume

Mean diameter	Bet surface area	Pore volume	References
34.66 Å	65.36 m^2/g	0.039 cm^3/g	Lataye et al. (2009)
42.60 Å	36.44 m^2/g	0.0388 cm^3/g	Srivastava et al. (2007)
–	480–600 m^2/g	–	Aghav et al. (2011)
56.93 Å	192.13 m^2/g	0.2735 mL/g	Imyim and Prapalimrungsi (2010)
34.66 Å	65.36 m^2/g	0.039 cm^3/g	Lataye et al. (2008)
42.603 Å	36.44 m^2/g	–	Srivastava et al. (2006)
–	10.995 m^2/g	0.038 mL/g	Kizito et al. (2015)
92 µm	62.8 m^2/g	–	Ganvir and Das (2011)

4 Preparation of silica and catalyst from RHA

Oxides of silica are the most abundant on the surface of the earth and it has many uses and it have been of great importance for the evolution of mankind, especially in the era of electronics and information technology where it is used extensively for making electronic circuits, transistors, diodes and also finds its use in ceramic and polymer industries (Liu et al. 2012). Silica also has many technological applications such as thixotropic agents, thermal insulators and composite filters mainly because of its small diameter (Soltani et al. 2015). Table 9 lists the various applications of silica and their acceptance in the market. In some applications like solar panel and semiconductor, silica has virtually no alternative, but use of silica as composite filter and polymer is relatively new and there still lies some hindrances to its proper use. The applications of silica in various other fields have been studied over the past decades.

Silica is abundantly available on the earth's surface as an oxide and it has so many uses in different industries. Even then silica used in these industries is prepared synthetically, making the end product costly (Londeree 2002). This is the main driving force for the search for alternate source of silica, and RHA plays an important role in this regard because of high silica content of rice husk (about 52 % by weight) (Liu et al. 2012). Recent studies demonstrated that RHA which contains about 95 % silica by weight and may be a source from which silica can be extracted very economically (Della et al. 2002). The RHA, abundantly available is refluxed with either nitric acid or hydrochloric acid to reduce metallic impurities present in it to a negligible level (Adam et al. 2013; Chang et al. 2006). The acid treated ash is directly dissolved to make sodium silicate which is then converted into silica by adding suitable amount of mineral acid. The various methods used for extraction of silica form RHA have been given in Table 10. The general procedure of extraction of silica follows the two basic reactions—Eqs. (9) and (10).

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O \tag{9}$$

$$Na_2SiO_3 + H_2SO_4 \rightarrow SiO_2 + Na_2SO_4 + H_2O \tag{10}$$

The prepared silica is usually amorphous in nature and that has been confirmed by the broad peak in the X-ray diffraction spectrograph. The XRD study of prepared silica has been studied by An et al. (2010). Figure 4 shows a broad peak around 22.5° which confirms the amorphous structure of silica (An et al.

Table 9 The different value added products which can be prepared from silica

Application	Characteristics	Market sector	References
Thixotropic agents, thermal insulators, composite fillers	Small-diameter	Electronics, ceramic and polymer material industries	An et al. (2010)
Refractory materials (silica bricks)	High strength under high temperatures	Coke ovens and glass furnaces manufacturing units	Pilate et al. (2015)
Drug delivery agent	Highly porous structure	Medical applications	Pijarn et al. (2010)
Biogenic silica nano-particles	Biocompatibility and bioactivity	Materials science and biomedicine fields	Alshatwi et al. (2015)
Adsorbent and catalyst	High specific surface area, large pore volume and chemical inertness	Wastewater treatment plants for different industries	Kim et al. (2014)

Table 10 Extraction of silica from rice husk ash using different processes

Methodology	Remarks	References
Carbon dioxide neutralization and precipitate separation processes	Yield of silica 72–98 %. Recovery rate of Na_2CO_3 92.25 %	Liu et al. (2011)
Carbonation method. Impregnation ratio of Na_2CO_3 to RHA (6:1). PEG is added	Yield of silica reached to 84.57 %. Hydrated silica powders with amorphous structure and high purity	An et al. (2011)
Alkaline extraction followed by acid precipitation	Pure silica with minimum mineral contamination. Yield of silica 91 %	Kalapathy et al. (2000)
Thermal degradation method	Superfine silica with a diameter 50 nm	Zhang et al. (2015)

2010; Kumar et al. 2015). Several other studies on XRD also indicated a broad peak at around 22°–23° which confirms the amorphous structure of silica and absence of any orderly crystalline structure (An et al. 2011;Liu et al. 2012). The SEM photograph of silica is given in Fig. 5 as given by An et al. 2011. Silica particles have diameter about 100–200 nm and are interlinked together. The particles appear to be spherical in nature and at magnification of 20 K the porous structures of silica are clearly revealed, the hexagonal pores observed are uniform and within the mesoporous range (Jullaphan et al. 2009; Kumar et al. 2015).

This method of silica preparation from RHA, as given by Adam and Fua (2008), is modified to form catalysts. A scheme of simultaneous preparation of activated carbon and silica as given by Liu et al. (2011) is shown in Fig. 6. The incorporation of metals onto silica to prepare catalyst was undertaken via sol–gel techniques as more control on final properties of the catalyst to be prepared can be attained by using sol–gel technique, because of the ability of metal precursor to mix homogeneously with molecular precursor of the support i.e. silica (Lambert and Gonzalez 2001). Several researches have been carried out to obtain silica based catalyst by impregnation of metals onto silica. Nickel nitrate was incorporated into silica matrix via ion exchange, in accordance to Chang et al. (2001). By the deposition–precipitation method copper nitrate was introduced in RHA (Chen et al. 2010).

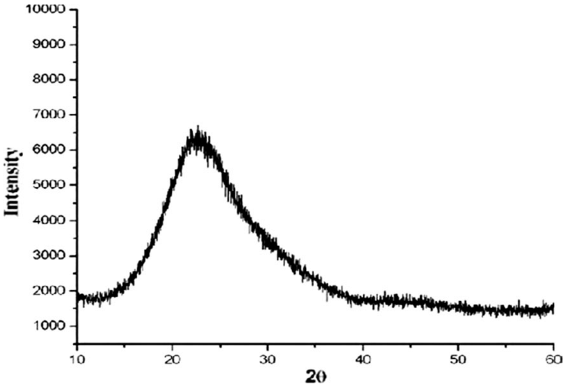

Fig. 4 X-ray diffraction pattern of silica produced from RHA (An et al. 2010)

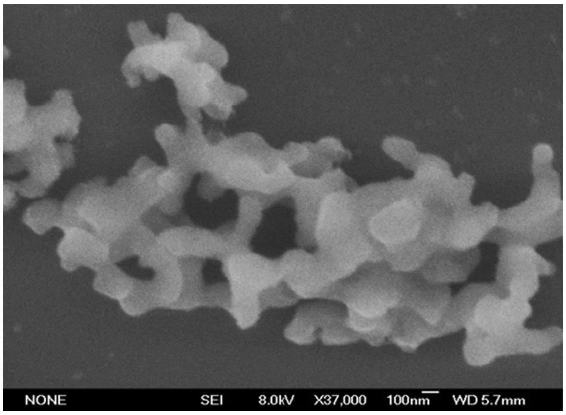

Fig. 5 SEM photographs of silica prepared form rice husk ash (An et al. 2011)

Metals are usually impregnated onto silica for the purpose of preparation of catalyst. The metals that are chosen are usually transition metals such as chromium, molybdenum and tungsten and even iron. (Adam and Iqbal 2011). A sol–gel technique is generally followed while preparing the catalyst. A suspension of the sodium silicate extracted from RHA is prepared and heated. To the suspension metal ions of calculated amount is added and stirred. Metal ions are usually in form of complex salts or nitrates such as $Fe(NO_3)_3{\cdot}9H_2O$. The metal ion is added drop wise such that the process of addition could be stopped when a certain pH is reached. The solution is precipitated, aged, washed and then calcinated at high temperature in a muffle furnace (Gan and Li 2013). The basic technique of preparation remains same although there might be some slight differences. Some of the different preparation method has been discussed in Table 11. Sol–gel technique is preferred generally over other methods because of the ability of the metal precursor to mix homogeneously with the suspension of silica i.e. the molecular precursor of the support (Jullaphan et al. 2009). Metal ions can be easily trapped in the polymerized gel allowing precipitation from the solution, where metals occupy neighbouring position in the gel, which leads to the formation of metal–oxygen–metal bonds under further processing like calcination at very high temperature (Namiki et al. 2005). Another common technique used is ion exchange method, where aqueous metal ions are used to produce metal/RHA via incipient wetness impregnation (Chang et al. 2001). Another technique used is deposition–precipitation to incorporate the metal nitrate into RHA, where metal salt is dissolved in urea solution and then added to the RHA suspension (Shen et al. 2014). The major area of interest for using catalyst is the selectivity of the catalyst activity and increased reaction rate. Major works in the field of

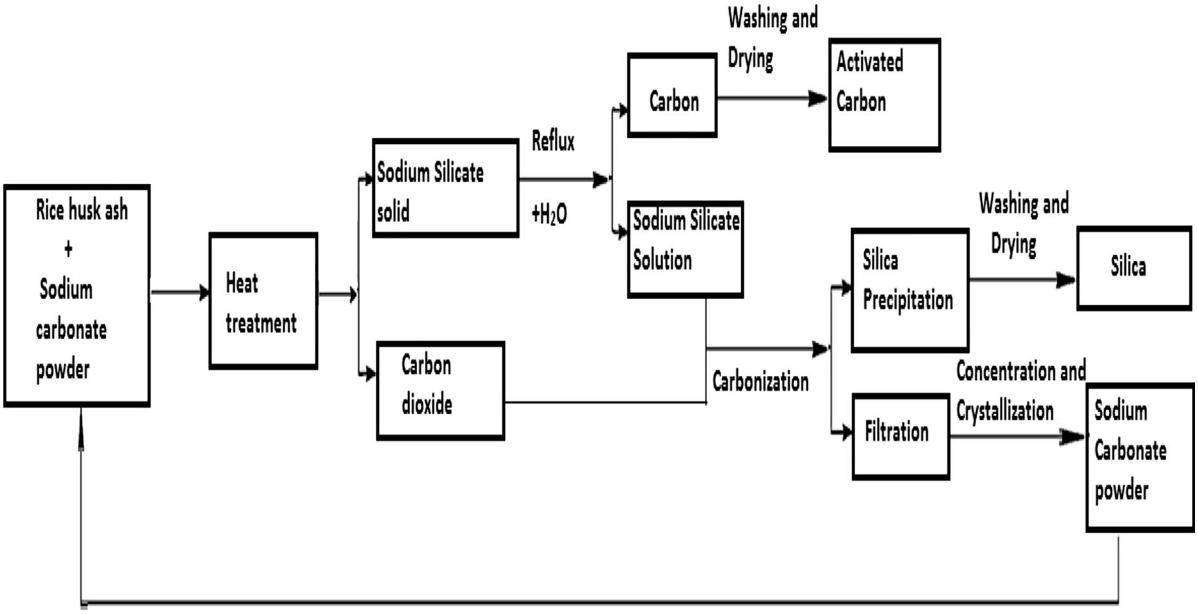

Fig. 6 Schematic representation of simultaneous production of silica and activated carbon from rice husk ash (Liu et al. 2011)

Table 11 Preparation of different silica supported catalyst from rice husk ash

Process	Reagent	Remarks	References
Incipient impregnation method. Sample dried at 105 °C, 12 h, followed by calcination at 500 °C, 4 h	$Fe(NO_3)_3\cdot 9H_2O$	96 % decolorization of acid red within 120 min	Daud and Hameed (2010)
Modified alkali extraction method	$Fe(NO_3)_3\cdot 9H_2O$	100 % decolorization of Rhodamine B after 10 min, pH 3	Gan and Li (2013)
Chromium incorporated silica matrix	HNO_3	99.9 % conversion of styrene into benzaldehyde	Adam and Iqbal (2011)
Incipient wetness impregnation. Sample calcined at 600 °C, 1 h	$Fe(NO_3)_3\cdot 9H_2O$, $Ni(NO_3)_2\cdot 6H_2O$	In situ catalytic conversion efficiency of tar is 92.3 %	Shen et al. (2014)
Direct incorporation of Indium ions onto silica	HNO_3	Benzylation of benzene, with 100 % conversion and 90 % selectivity for diphenyl methane	Adam and Ahmed (2008)
Deposition–precipitation technique	$Cu(NO_3)_2\cdot 5H_2O$	Partial oxidation of 87 % methanol conversion with 92.5 % H_2 and 2.9 % CO selectivity, respectively	Chen et al. (2010)

catalyst preparation have tried to optimize the weight percentage of metal ions impregnated onto silica matrix to provide best results. The operating condition in which the catalyst acts is also optimized to achieve maximum yield.

5 Emergence of RHA as a raw material for various other value added products

It is estimated in 2005, that globally 21 million tonnes of RHA per year (Namiki et al. 2005). In the last decade, the generation and discharge of RHA into the ecosystem has garnered ample criticism, mainly in lieu of its carcinogenic and bio-accumulative properties. The results of such discharge of RHA causes health related problems such as loss of appetite, fatigue, silicosis syndrome, respiratory disorders and even death (Zhang et al. 2015). Under such conditions, the cost associated with proper discharge of RHA in the developed countries was at its peak with approximated \$50 per tonne of discharge while it was lower in the developing countries with the cost ranging nearly around \$5 per tonne of RHA discharge. Hence, grew a general interest to convert this waste into some useful form, not only to decrease the value associated with its proper disposal but also generate products having economic importance in the world market. (Bronzeoak Ltd. 2003; Siriwandena et al. 2001). Under such ideology to generate valuable product, RHA finds its application as a pozzolanic material for the manufacture of high strength concrete and refractory bricks (Hwang and Huynh 2015), a feedstock for the silicon chip processing industry (Watari et al. 2006). It find its application as refractory powder, for vulcanizing rubber, as an agent for beer clarification, as filler in polymer production and as oil adsorbent (Bronzeoak Ltd. 2003; Siriwandena et al. 2001). Among these, the two most important use of RHA has been in the steel industry as an insulator and as a pozzolan in the concrete industry (Bronzeoak Ltd. 2003; Siriwandena et al. 2001). RHA has excellent insulating property, having low thermal conductivity, low bulk density and high melting point. Its insulating property makes its use possible as an excellent ‘tundish powder’—powders that are used to insulate the tundish to prevent rapid cooling of steel to ensure uniform solidification in continuous casting process (Watkinson 2002). In the concrete making process, RHA was initially used for the purpose of lowering the price of concrete, as ordinary portland cement is expensive. Later, studies found that addition of RHA not only make the concrete making process economic but also alters some properties of the concrete like reduction of setting time, increase in compressive strength and increase chemical resistance mainly prevents chloride penetration. The pozzolan properties of RHA is mainly due to these factor; the silica content, crystalline state of silica, size and surface area of the rice husk particles. (Zain et al. 2011*)*. RHA having such properties can be prepared by suitable incineration under controlled temperature in

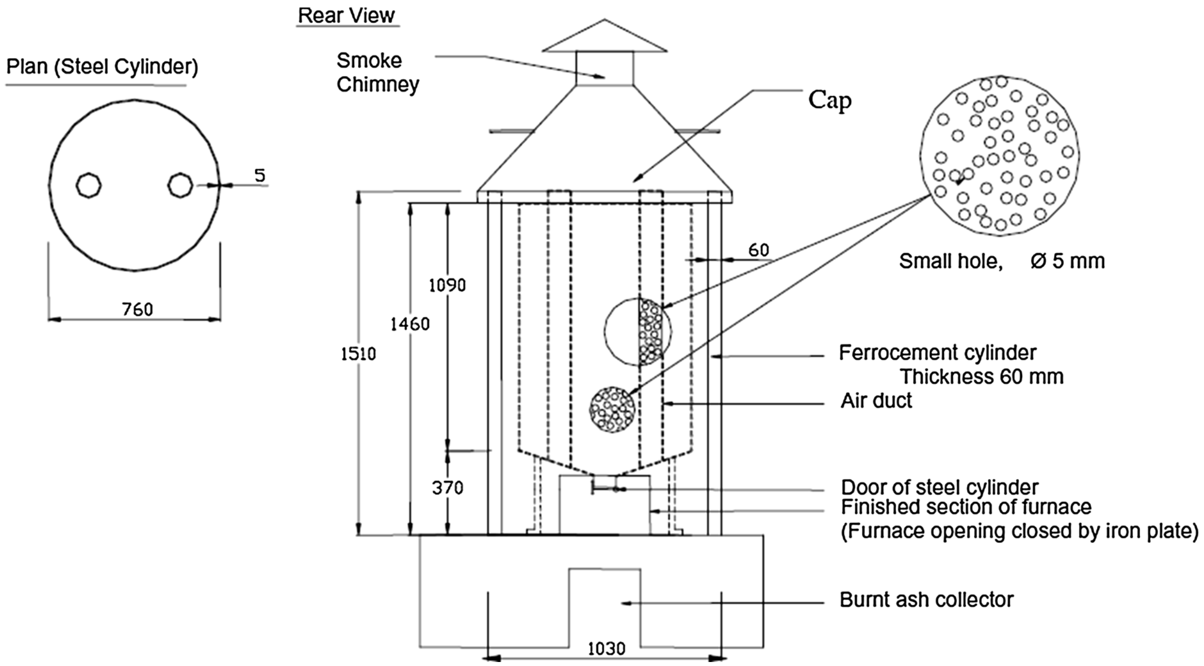

Fig. 7 Design of a furnace for the proper incineration of rice husk to produce proper ash for the use in concrete making (Zain et al. 2011)

properly designed furnace and proper grinding process (Mehta 1989). Figure 7 shows a furnace that has been designed (Zain et al. 2011), after reviewing the furnaces reported by Loo et al. (1984) and Ramli (1993). The furnace has two sections; a ferro-cement section of diameter 1030 mm whose purpose is to trap the heat and prevent it from escaping into the atmosphere and there is a steel cylinder of 5 mm thickness and diameter 760 mm which acts as a container for the rice husk (Zain et al. 2011). Other less popular uses of RHA is its application in the manufacture of refractory bricks, light weight insulating boards and as a raw material for silicon chip manufacturing (Armestoa et al. 2002). The market has not been fully established to meet the expected potential of using RHA for the above mentioned purpose. The potential market for the use of RHA is predominantly found in the steel industries, but its expansion is hindered due to health related issues associated with the use of ash (Siriwandena et al. 2001). Thus more research in this regard need to be carried out. RHA's concrete market is established and is expanding keeping in line with its potential. The various other uses of RHA, their potential for commercial use and their current development is given in Table 12 (Bronzeoak Ltd. 2003). In spite of having so much potential of being the raw material for the preparation of numerous valuable products, the present utilization of RHA is limited to cheap concrete blocks and tundish powder for iron and steel industries (Fig. 8).

6 Challenges and future prospects

The benefits of RHA in steel and concrete industry has been well established, but there exists other enormous applications which are exhibiting promising potential to be commercially utilized all over the world. Currently, energy from biomass is estimated to contribute about 9–13 % of the global energy supply (UNDP 2000). Rice husk having high calorific value can contribute to this energy market, as it releases energy (13.6 MJ/kg) when converted from husk to ash (Armestoa et al. 2002). Asian farmers use RHA to prevent insect attack in stored food and few scientific research have been undertaken to identify the efficacy of it as preservative (Saha et al. 2001). The high carbon content in RHA can be utilized as a natural adsorbent for purification of wastewater. There are many scientific studies in this regard even though the adsorbent is

Table 12 Opportunity matrix of uses and potential markets for RHA (Foo and Hameed 2009d)

Application	Current state of development	Current demand	Potential demand	Geographical use	Purchase price per tonne	Suitability as a market
Flat steel production	Market already in existence	Medium	Decreasing	World wide	Medium	Not expanding
Concrete manufacture	Market in existence, and ongoing research	Low to medium	High	World wide	Low	Expanding and CER potential
Silica fume replacement	Market in existence, and ongoing research	Low	High	World wide	High	Expanding and CER potential
Lightweight construction materials	Market in existence, and ongoing research	Low	Low to medium	World wide	Low	Currently localized, potential in future

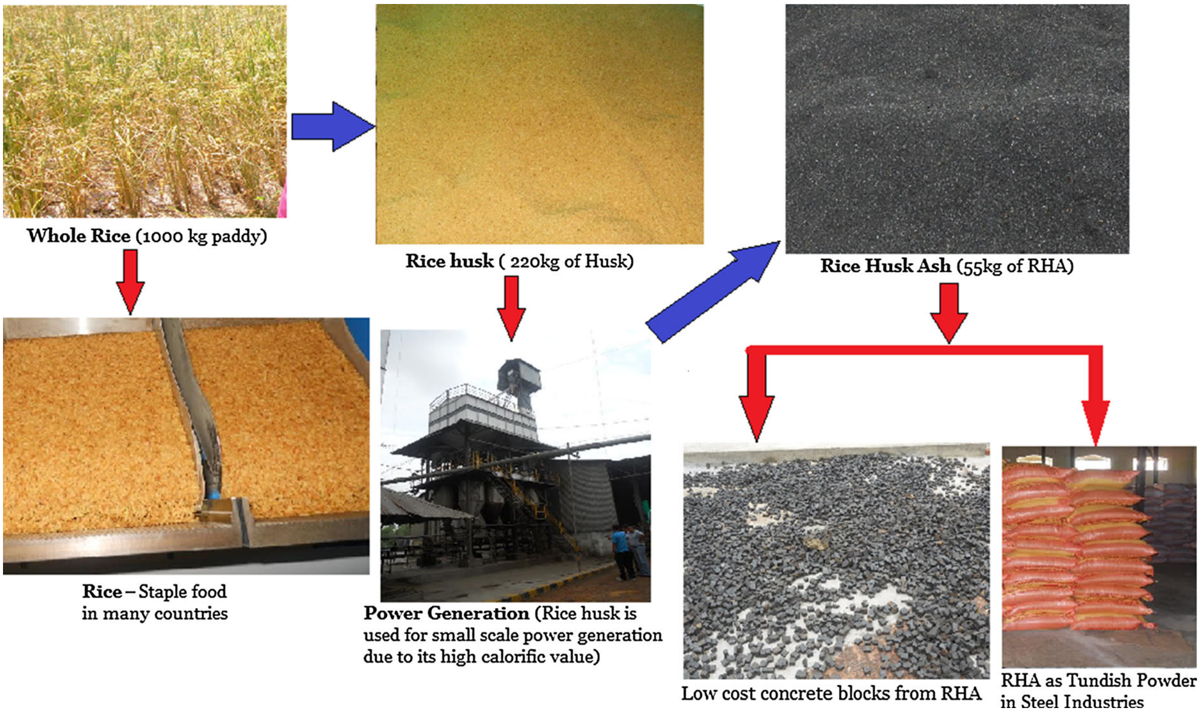

Fig. 8 Present day scenario of utilization of rice and RHA

more economic in comparison to commercially available activated carbon, it has not found its rightful commercial market. This may be due to the lack of research to establish a proper large scale unit for preparation of adsorbent. Greenwich University is studying small scale rice mill in Bangladesh and Vietnam for establishing RHA as an adsorbent to purify water. Reports suggest that RHA can be used as soil ameliorant for the purpose of breaking up clay (Confidential Report 1998). RHA has been used to vulcanize rubber but its market has not been properly established due to lack of research to give a scheme of a large scale unit. Rice husk which has been slowly incinerated over 6 months is used to absorb oil in California. The potential market for RHA in the silicon chip industry is huge and still expanding. However, technique of extracting silica from ash has not yet been established fully on a large scale and it might be many years before its application is market ready. The future looks very bright for RHA to be used

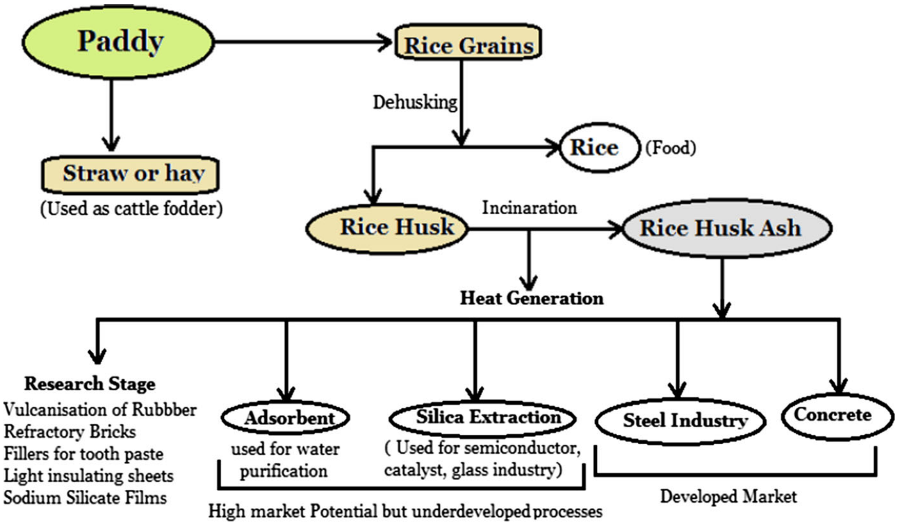

Fig. 9 Possible value added products from rice husk ash and their potential in market and stage of development

commercially, particularly as an adsorbent and a source for silica provided proper research is carried out to give a scheme of feasible large scale economically viable process. The other uses of RHA which are still in research stage are—manufacture of roof tiles, production of sodium silicate films, extended fillers for paints, abrasive filler for tooth paste, free running agent in fire extinguishers. (Confidential Report 1998; Kalapathy et al. 2000). Figure 9 shows graphically the various possible value added products that can be derived from RHA and their current state of development and potential in market. The challenges in utilization of RHA to its full potential are due to different socio- economic problems and inactiveness from the concerned authority. Various causes for improper utilization of RHA in developing countries are (a) Information: lack of information about potential of RHA, inefficient information transfer about the utility of RHA (b) Environmental concerns: lack of environmental concerns by individuals, absence of proper environmental laws and their proper implementation (c) Active participation: lack of initiatives by concerned authorities, social and political issues hinders implementation of new ideas.

7 Conclusion

Wastewater treatment is a subject of concern especially due to the complexity, efficiency and cost involved with the process. In this context, adsorption provides a possible solution to the problem of water treatment and RHA has a huge potential to be an efficient and economic adsorbent and in turn solve the problem of its disposal into the environment and provide an effective scope for recycle of RHA. The high silica content of RHA also instigated the researchers to investigate it as a possible source of silica and silica based catalysts. The results were overwhelming and the researches in the past one decade have proved that its future market potential is huge. Big silicon chip producing firms have started investigating its possible use as raw material for generating silica. Although RHA has stable market in accordance to its potential in the concrete and steel industries, as an adsorbent and raw material for producing silica is yet to be stabilized and this may be accounted to the lack of proper large scale scheme for the production from ash. Many other usefulness of RHA is also being explored like its use as filler in paint and toothpaste, production of sodium silicate films, roof tiles and insulating sheets. In a world with depleting oil reserve, energy from biomass of rice husk could be well utilized to generate energy. The literary review provides an effective scheme to utilize rice husk to derive different value added products which are of paramount importance. The methods discussed not only provide scheme to produce economically valuable products but also revealed an effective solution to the problem associated with its proper disposal through superior recycle of this agricultural waste.

Acknowledgments The authors are thankful to Professor T. Kumar, Director of NIT Durgapur for providing us access to the necessary facilities which are required for proper completion of this research work. Authors would also like to thank Miss Monica Meena and Mr. Shubhrojyoti Laha, Department of Chemical Engineering, NIT Durgapur for all kind of cooperation and immense support.

References

Abo-El-Enein SA, Eissa MA, Diafullah AA, Rizk MA, Mohamed FM (2009) Removal of some heavy metals ions from wastewater by copolymer of iron and aluminum impregnated with active silica derived from rice husk ash. J Hazard Mater 172:574–579. doi:10.1016/j.jhazmat.2009.07.036

Adam F, Ahmed AE (2008) The benzylation of xylenes using heterogeneous catalysts from rice husk ash silica modified with gallium, indium and iron. Chem Eng J 145:328–334. doi:10.1016/j.cej.2008.08.028

Adam F, Fua HK (2008) Production of silica from biogenic material. Malaysian Patent MY-136715-A

Adam F, Iqbal A (2011) Silica supported amorphous molybdenum catalysts prepared via sol–gel method and its catalytic activity. Microporous Mesoporous Mater 141(1–3):119–127. doi:10.1016/j.micromeso.2010.10.037

Adam F, Appaturi JN, Iqbal A (2012) The utilization of rice husk silica as a catalyst: review and recent progress. Catal Today 190(1):2–14. doi:10.1016/j.cattod.2012.04.056

Adam F, Appaturi JN, Khanam Z, Thankappan R, Nawi MAM (2013) Utilization of tin and titanium incorporated rice husk silica nanocomposite as photocatalyst and adsorbent for the removal of methylene blue in aqueous medium. Appl Surf Sci 264:718–726. doi:10.1016/j.apsusc.2012.10.106

Aghav RM, Kumar S, Mukherjee SN (2011) Artificial neural network modeling in competitive adsorption of phenol and resorcinol from water environment using some carbonaceous adsorbents. J Hazard Mater 188(1–3):67–77. doi:10.1016/j.jhazmat.2011.01.067

Ahmaruzzaman M (2010) A review on the utilization of fly ash, progress in energy and combustion science. Prog Energ Combust 36:327–363. doi:10.1016/j.pecs.2009.11.003

Akhtar M, Bhanger MI, Iqbal S, Hasany SM (2006) Sorption potential of rice *husk* for the removal of 2,4-dichlorophenol from aqueous solution: kinetic and thermodynamic investigations. J Hazard Mater 128:44–52. doi:10.1016/j.jhazmat.2005.07.025

Akhtar M, Iqbal S, Kausar A, Bhanger MI, Shaheen MA (2010) An economically viable method for the removal of selected divalent metal ions from aqueous solutions using activated rice husk. Colloids Surf B 75(1):149–155. doi:10.1016/j.colsurfb.2009.08.025

Alshatwi AA, Athinarayanan J, Periasamy VS (2015) Biocompatibility assessment of rice husk-derived biogenic silica nanoparticles for biomedical applications. Mater Sci Eng C 47:8–16. doi:10.1016/j.msec.2014.11.005

An D, Guo Y, Zhu Y, Wang Z (2010) A green route to preparation of silica powders with rice husk ash and waste gas. Chem Eng J 162:509–514. doi:10.1016/j.cej.2010.05.052

An D, Guo Y, Zou B, Zhu Y, Wang Z (2011) A study on the consecutive preparation of silica powders and active carbon from rice husk ash. Biomass Bioenergy 35:1227–1234. doi:10.1016/j.biombioe.2010.12.014

Armestoa L, Bahilloa A, Veijonenb K, Cabanillasa A, Oteroa J (2002) Combustion behaviour of rice husk in a bubbling fluidized bed. Biomass Bioenergy 23(3):171–179. doi:10.1016/S0961-9534(02)00046-6

Ayswarya EP, Vidya Francis KF, Renju VS, Thachil ET (2012) Rice husk ash—a valuable reinforcement for high density polyethylene. Mater Des 41:1–7. doi:10.1016/j.matdes.2012.04.035

Beagle EC (2006) Rice husk conversion to energy. FAO, Rome

Bhagiyalakshmi M, Yun LJ, Anuradha R, Jang HT (2009) Utilization of rice husk ash as silica source for the synthesis of mesoporous silicas and their application to CO_2 adsorption through TREN/TEPA grafting. J Hazard Mater 175:928–938. doi:10.1016/j.jhazmat.2009.10.097

Bhattacharya AK, Mandal SN, Das SK (2006) Adsorption of Zn(II) from aqueous solution by using different adsorbents. Chem Eng J 123:43–51. doi:10.1016/j.cej.2006.06.012

Bronzeoak Ltd. (2003) Rice husk ash market study. http://www.webarchive.nationalarchives.gov.uk/20090609003228/http://www.berr.gov.uk/files/file15138.pdf. Accessed Jan 2015

Chakraborty S, Chowdhury S, Saha PD (2011) Adsorption of crystal violet from aqueous solution onto NaOH-modified rice husk. Carbohydr Polym 86:1533–1541. doi:10.1016/j.carbpol.2011.06.058

Chang FW, Tsay MT, Liang SP (2001) Hydrogenation of CO_2 over nickel catalysts supported on rice husk ash prepared by ion exchange. Appl Catal A Gen 209:217–227. doi:10.1016/S0926-860X(00)00772-9

Chang FW, Yang HC, Roselin LS, Huo WY (2006) Ethanol dehydrogenation over copper catalysts on rice husk ash prepared by ion exchange. Appl Catal A Gen 304:30–39. doi:10.1016/j.apcata.2006.02.017

Chatterjee S, Kumar A, Basu S, Dutta S (2012) Application of response surface methodology for methylene blue dye removal from aqueous solution using low cost adsorbent. Chem Eng J 181–182:289–299. doi:10.1016/j.cej.2011.11.081

Chaudhary DS, Jollands MC (2004) Characterization studies of rice hull ash. J Appl Polym Sci 93(1):1–8. doi:10.1002/app.20217

Chaudhary DS, Jollands MC, Cser F (2002) Understanding rice hull ash as fillers in polymers: a review. Silicon Chem 1:281–289. doi:10.1023/B:SILC.0000018361.66866.80

Chen WS, Chang FS, Roselin LS, Ou TC, Lai SC (2010) Partial oxidation of methanol over copper catalysts supported on rice husk ash. J Mol Catal A Chem 318(1–2):36–43. doi:10.1016/j.molcata.2009.11.005

Chen Y, Zhu Y, Wang Z, Li Y, Wang L, Ding L, Gao X, Ma Y, Guo Y (2011) Application studies of activated carbon derived from rice husks produced by chemical-thermal process—a review. Adv Colloid Interfac 163:39–52. doi:10.1016/j.cis.2011.01.006

Chingombe P, Saha B, Wakeman RJ (2005) Surface modification and characterization of a coal-based activated carbon. Carbon 43:3132–3143. doi:10.1016/j.carbon.2005.06.021

Confidential Report (1998) Rice husk ash market assessment, Bangkok, Thailand

Daifullah A, Girgis B, Gad H (2004) A study of the factors affecting the removal of humic acid by activated carbon prepared from biomass material. Colloids Surf A 235:1–10. doi:10.1016/j.colsurfa.2003.12.020

Dasgupta J, Kumar A, Mandal DD, Mandal T, Datta S (2015) Removal of phenol from aqueous solutions using adsorbents derived from low-cost agro-residues. Desalin Water Treat (accepted). doi:10.1080/19443994.2015.1061455

Daud NK, Hameed BH (2010) Decolorization of Acid Red 1 by Fenton-like process using rice husk ash-based catalyst. J Hazard Mater 176:938–944. doi:10.1016/j.jhazmat.2009.11.130

de Yuso AM, Rubio B, Izquierdo MT (2014) Influence of activation atmosphere used in the chemical activation of almond shell on the characteristics and adsorption performance of activated carbons. Fuel Process Technol 119:74–80. doi:10.1016/j.fuproc.2013.10.024

Della VP, Kühn I, Hotza D (2002) Rice husk ash as an alternate source for active silica production. Mater Lett 57:818–821. doi:10.1016/S0167-577X(02)00879-0

Doke KM, Khan EM (2013) Adsorption thermodynamics to clean up wastewater; critical review. Rev Environ Sci Biotechnol 12:25–44. doi:10.1007/s11157-012-9273-z

Foo KY, Hameed BH (2009a) A short review of activated carbon assisted electrosorption process: an overview, current stage and future prospects. J Hazard Mater 170:552–559. doi:10.1016/j.jhazmat.2009.05.057

Foo KY, Hameed BH (2009b) Recent developments in the preparation and regeneration of activated carbons by microwaves. Adv Colloid Interface Sci 149:19–27. doi:10.1016/j.cis.2008.12.005

Foo KY, Hameed BH (2009c) Utilization of biodiesel waste as a renewable resource for activated mcarbon: application to environmental problems. Renew Sustain Energy Rev 13(9):2495–2504. doi:10.1016/j.rser.2009.06.009

Foo KY, Hameed BH (2009d) Utilization of rice husk ash as novel adsorbent: a judicious recycling of the colloidal agricultural waste. Adv Colloid Interfac Sci 152:39–47. doi:10.1016/j.cis.2009.09.005

Gan PP, Li SFY (2013) Efficient removal of Rhodamine B using rice hull-based silica supported iron catalyst by Fenton-like process. Chem Eng J 229:351–363. doi:10.1016/j.cej.2013.06.020

Ganvir V, Das K (2011) Removal of fluoride from drinking water using aluminium hydroxide coated rice husk ash. J Hazard Mater 185(2–3):1287–1294. doi:10.1016/j.jhazmat.2010.10.044

Gastaldini ALG, Isaia GC, Saciloto AP, Missau F, Hoppe TF (2010) Influence of curing time on the chloride penetration resistance of concrete containing rice husk ash: a technical and economical feasibility study. Cem Concr Compos 32:783–793. doi:10.1016/j.cemconcomp.2010.08.001

Gupta VK, Ali I, Jain CK, Sharma M, Saini VK (2003) Removal of cadmium and nickel from wastewater using bagasse fly ash—a sugar industry waste. Water Res 37:4038–4044. doi:10.1016/S0043-1354(03)00292-6

Hwang C, Huynh T (2015) Investigation into the use of unground rice husk ash to produce eco-friendly construction bricks. Constr Build Mater 93:335–341. doi:10.1016/j.conbuildmat.2015.04.061

Imyim A, Prapalimrungsi E (2010) Humic acids removal from water by α-aminopropyl functionalized rice husk ash. J Hazard Mater 184:775–781. doi:10.1016/j.jhazmat.2009.02.140

Jain R, Mathur M, Sikarwar S, Mittal A (2007) Removal of the hazardous dye rhodamine B through photocatalytic and adsorption treatments. J Environ Manag 85:956–964. doi:10.1016/j.jenvman.2006.11.002

Jayaranjan MLD, van Hullebusch ED, Annachhatre AP (2014) Reuse options for coal fired power plant bottom ash and fly ash. Rev Environ Sci Biotechnol 13:467–486. doi:10.1007/s11157-014-9336-4

Jullaphan O, Witoon T, Chareonpanich M (2009) Synthesis of mixed-phase uniformly infiltrated SBA-3-like in SBA-15 bimodal mesoporous silica from rice husk ash. Mater Lett 63:1303–1306. doi:10.1016/j.matlet.2009.03.001

Kalapathy U, Proctor A, Shultz J (2000) A simple method for production of pure silica from rice hull ash. Bioresour Technol 73:257–262. doi:10.1016/S0960-8524(99)00127-3

Kim Y, Bae J, Park J, Suh J, Lee S, Park H, Choi H (2014) Removal of 12 selected pharmaceuticals by granular mesoporous silica SBA-15 in aqueous phase. Chem Eng J 256:475–485. doi:10.1016/j.cej.2014.06.100

Kizito S, Wu S, KipkemoiKirui S, Lei M, Lu Q, Bah H, Dong R (2015) Evaluation of slow pyrolyzed wood and rice husks biochar for adsorption of ammonium nitrogen from piggery manure anaerobic digestate slurry. Sci Total Environ 505:102–112. doi:10.1016/j.scitotenv.2014.09.096

Kumar A, Gupta D (2015) Behavior of cement-stabilized fiber-reinforced pond ash, rice husk ash–soil mixtures. Geotext Geomembr. doi:10.1016/j.geotexmem.2015.07.010

Kumar P, Prasad B, Chand S (2009) Treatment of desizing wastewater by catalytic thermal treatment and coagulation. J Hazard Mater 163:433–440. doi:10.1016/j.jhazmat.2008.06.114

Kumar A, Singha S, Dasgupta D, Datta S, Mandal T (2015) Simultaneous recovery of silica and treatment of rice mill wastewater using rice husk ash: an economic approach. Ecol Eng 84(2015):29–37. doi:10.1016/j.ecoleng.2015.07.010

Lakshmi UR, Srivastava VC, Mall ID, Lataye DH (2009) Rice husk ash as an effective adsorbent: evaluation of adsorptive characteristics for Indigo Carmine dye. J Environ Manag 90:710–720. doi:10.1016/j.jenvman.2008.01.002

Lambert CK, Gonzalez RD (2001) The effect of pH and metal loading on the properties of sol–gel Rh/SiO. J Solid Chem 158:154–161. doi:10.1006/jssc.2001.9086

Lataye DH, Mishra IM, Mall ID (2008) Pyridine sorption from aqueous solution by rice husk ash (RHA) and granular activated carbon (GAC): parametric, kinetic, equilibrium and thermodynamic aspects. J Hazard Mater 154:858–870. doi:10.1016/j.jhazmat.2007.10.111

Lataye DH, Mishra IM, Mall ID (2009) Adsorption of α-picoline onto rice husk ash and granular activated carbon from aqueous solution: equilibrium and thermodynamic study. Chem Eng J 147:139–149. doi:10.1016/j.cej.2008.06.027

Le HT, Siewert K, Ludwig H (2015) Alkali silica reaction in mortar formulated from self-compacting high performance concrete containing rice husk ash. Constr Build Mater 88:10–19. doi:10.1016/j.conbuildmat.2015.04.005

Liu Y, Guo Y, Zhu Y, An D, Gao W, Wang Z, Ma Y, Wang Z (2011) A sustainable route for the preparation of activated carbon and silica from rice husk ash. J Hazard Mater 186:1314–1319. doi:10.1016/j.jhazmat.2010.12.007

Liu Y, Guo Y, Gao W, Wang Z, Ma Y, Wang Z (2012) Simultaneous preparation of silica and activated carbon from rice husk ash. J Clean Prod 32:204–209

Londeree DJ (2002) Silica–titania composites for water treatment. M.Eng. Thesis, University of Florida

Loo YC, Nimityongskul P, Karasudhi P (1984) Economical rice husk-ash concrete. Build Res Pract 12(4):233–238

Martin JI (1938) MS thesis, Louisiana State University, USA

Mehta PK (1989) Rice husk ash as a mineral admixture in concrete. In: Proceedings of the 2nd international seminar on durability of concrete: aspects of admixtures and industrial by-products, vol 13. Gothenburg, Sweden, pp 1–6

Mitchell LD, Beaudoin JJ, Grattan-Bellew P (2004) The effects of lithium hydroxide solution on alkali silica reaction gels created with opal. Cem Concr Res 34:641–649. doi:10.1016/j.cemconres.2003.10.011

Mutuk T, Mesci B (2014) Analysis of mechanical properties of cement containing boron waste and rice husk ash using full factorial design. J Clean Prod 69:128–132. doi:10.1016/j.jclepro.2014.01.051

Naiya TK, Bhattacharya AK, Mandal S, Das SK (2009) The sorption of lead(II) ions on rice husk ash. J Hazard Mater 163(2–3):1254–1264. doi:10.1016/j.jhazmat.2008.07.119

Nakbanpote W, Goodman BA, Thiravetyan P (2007) Copper adsorption on rice husk derived materials studied by EPR and FTIR. Colloids Surf A 304(1–3):7–13. doi:10.1016/j.colsurfa.2007.04.013

Namiki M, Ma JF, Iwashita T (2005) Identification of the silicon form in xylem sap of rice (*Oryza sativa* L.). Plant Cell Physiol 46(2):279–283

Nandi BK, Goswami A, Purkait MK (2009) Adsorption characteristics of brilliant green dye on kaolin. J Hazard Mater 161:387–395. doi:10.1016/j.jhazmat.2008.03.110

Patel M (2012) Potential of fruit and vegetable wastes as novel biosorbents: summarizing the recent studies. Rev Environ Sci Biotechnol 11:365–380. doi:10.1007/s11157-012-9297-4

Patel M, Karera A, Prasanna P (1987) Effect of thermal and chemical treatments on carbon and silica contents in rice husk. J Mater Sci 22:2457–2464. doi:10.1007/BF01082130

Pijarn N, Jaroenworaluck A, Sunsaneeyametha W, Stevens R (2010) Synthesis and characterization of nanosized-silica gels formed under controlled conditions. Powder Technol 203:462–468. doi:10.1016/j.powtec.2010.06.007

Pilate P, Lardot V, Cambier F, Brochen E (2015) Contribution to the understanding of the high temperature behavior and of the compressive creep behavior of silica refractory materials. J Eur Ceram Soc 35:813–822. doi:10.1016/j.jeurceramsoc.2014.09.019

Ramli M (1993) Durability of ferro-cement floating structures containing rice husk ash. In: Proceedings of the fourth international conference on structural failure, durability and retrofitting, Singapore, pp 289–294

Rao GR, Sastry ARK, Rohatgi PK (1989) Nature and reactivity of silica available in rice husk and its ashes. Bull Mater Sci 12:469–479. doi:10.1007/BF02744917

Rice Husk Ash (2011) http://www.Ricehuskash.com/details.htm. Retrieved on 13 Jan 2015

Rice Market Monitor (2010) Rice market monitor, trade and markets division, food and agriculture organization of the United Nations 13:1–37

Rocha CG, Zaia DAM, Alfaya RVS, Alfaya AAS (2009) Use of rice straw as biosorbent for removal of Cu(II), Zn(II), Cd(II) and Hg(II) ions in industrial effluents. J Hazard Mater 166:383–388. doi:10.1016/j.jhazmat.2008.11.074

Rosa SML, Rehman N, de Miranda MIG, Nachtigall SMB, Bica CID (2012) Chlorine-free extraction of cellulose from rice husk and whisker isolation. Carbohydr Polym 87:1131–1138. doi:10.1016/j.carbpol.2011.08.084

Roskill (2009) International metals and mineral information services. July 2009. http://www.roskill.com/reports/activated. Retrieved on 12 Jan 2015

Saha JC, Dikshit K, Bandyopadhyay M (2001) Comparative studies for selection of technologies for arsenic removal from drinking water. BUET-UNU International Workshop on Technologies for Arsenic Removal from Drinking Water, Bangladesh. http://www.sdnbd.org/sdi/issues/arsenic/BUET-UNU-arsenic-workshop.htm. Retrieved on 12 Jan 2015

Sharma YC, Uma (2010) Optimization of parameters for adsorption of methylene blue on a low cost activated carbon. J Chem Eng Data 55:435–439. doi:10.1021/je900408s

Sharma NK, Williams WS, Zangvil A (1984) Formation and structure of silicon carbide whiskers from rice hulls. J Am Ceram Soc 67(11):715–720. doi:10.1111/j.1151-2916.1984.tb19507.x

Sharma P, Kaur R, Baskar C, Chung WJ (2010) Removal of methylene blue from aqueous waste using rice husk and rice husk ash. Desalination 259:249–257. doi:10.1016/j.desal.2010.03.044

Shen Y, Zhao P, Shao Q, Takahashi F, Yoshikawa K (2014) In situ catalytic conversion of tar using rice husk char/ash supported nickel–iron catalysts for biomass pyrolytic gasification combined with the mixing-simulation in fluidized-bed gasifier. Appl Energy. doi:10.1016/j.apenergy.2014.10.074

Shi W, Wang S, Yang Q (2010) Climate change and global warming. Rev Environ Sci Biotechnol 9:99–102. doi:10.1007/s11157-010-9206-7

Siriwandena S, Ismail H, Ishakiaku US (2001) A comparison of white rice husk ash and silica as fillers in ethylene–propylene–dieneter polymer vulcanizates. Poly Int 50(6):707–713. doi:10.1002/pi.691

Soltani N, Bahrami A, Pech-Canul MI, González LA (2015) Review on the physicochemical treatments of rice husk for production of advanced materials. Chem Eng J 264:899–935. doi:10.1016/j.cej.2014.11.056

Song Y, Ding S, Chen S, Xu H, Mei Y, Ren J (2015) Removal of malachite green in aqueous solution by adsorption on sawdust. Korean J Chem Eng. doi:10.1007/s11814-015-0103-1

Srivastava VC, Mall ID, Mishra IM (2006) Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA. J Hazard Mater 134(1–3):257–267. doi:10.1016/j.jhazmat.2005.11.052

Srivastava VC, Mall ID, Mishra IM (2007) Adsorption thermodynamics and isosteric heat of adsorption of toxic metal ions onto bagasse fly ash (BFA) and rice husk ash (RHA). Chem Eng J 132(1–3):267–278. doi:10.1016/j.cej.2007.01.007

Tavlieva MP, Genieva SD, Georgieva VG, Vlaev LT (2013) Kinetic study of brilliant green adsorption from aqueous solution onto white rice husk ash. J Colloid Interface Sci 409:112–122. doi:10.1016/j.jcis.2013.07.052

Tiwari DP, Singh DK, Saksena DN (1995) Hg(II) adsorption from aqueous solutions using rice-husk ash. J Environ Eng 121:479–481. doi:10.1061/(ASCE)0733-9372(1995)121:6(479)

Totlani K, Mehta R, Mandavgane SA (2012) Comparative study of adsorption of Ni(II) on RHA and carbon embedded silica obtained from RHA. Chem Eng J 181–182:376–386. doi:10.1016/j.cej.2011.11.099

UNDP (2000) United Nations Development Programme: World energy assessment. United States, New York

Van V, Rößler C, Bui D, Ludwig H (2014) Rice husk ash as both pozzolanic admixture and internal curing agent in ultra-high performance concrete. Cem Concr Compos 53:270–278. doi:10.1016/j.cemconcomp.2014.07.015

Watari T, Nakata A, Kiba Y, Torikai T, Yada M (2006) Fabrication of porous SiO_2/C composite from rice husks. J Eur Ceram Soc 26:797–801. doi:10.1016/j.jeurceramsoc.2005.06.013

Watkinson H (2002) Personal communication. CORUS, Teeside Technology Centre

Yeletsky PM, Yakovlev VA, Melgunov MS, Parmon VN (2009) Synthesis of mesoporous carbons by leaching out natural silica templates of rice husk. Microporous Mesoporous Mater 121(1–3):34–40. doi:10.1016/j.micromeso.2008.12.025

Zain MFM, Islam MN, Mahmud F, Jamil M (2011) Production of rice husk ash for use in concrete as a supplementary cementitious material. Constr Build Mater 25:798–805. doi:10.1016/j.conbuildmat.2010.07.003

Zhang H, Ding X, Chen X, Ma Y, Wang Z, Zhao X (2015) A new method of utilizing rice husk: consecutively preparing D-xylose, organosolv lignin, ethanol and amorphous superfine silica. J Hazard Mater 291:65–73. doi:10.1016/j.jhazmat.2015.03.003