Review Article Open Access

Wee-Keat Cheah, Chee-Heong Ooi, and Fei-Yee Yeoh*

Rice husk and rice husk ash reutilization into nanoporous materials for adsorptive biomedical applications: A review

DOI 10.1515/mesbi-2016-0004

Received February 15, 2016; revised July 25, 2016; accepted July 26, 2016

Abstract: The continuous generation of rice husk biomass makes this waste biomass a consistent and renewable resource for carbon zero power generation. Biochar from the power generation industry could be further utilized and converted into activated carbon through a simple activation process, foregoing the conventional carbonization process. Complete combustion of rice husk into rice husk ash could be subsequently processed into sodium silicate with little difficultly since more than 90 % of the rice husk ash constituent is silica. Sodium silicate is used mainly as a precursor for both the synthesis of mesoporous silica and zeolite. This paper reviews on the various nanoporous adsorbents derived from a single rice husk biomass.

Keywords: Rice husk, activated carbon, silica, zeolites, nanoporous adsorbent

1 Introduction

Rice is a cereal grain widely consumed by a large part of the world's human population especially in Asian countries. The protective outer layer of the grain, which is commonly known as rice husk (RH), is generated as a by-product from rice mills. The annual world rice production is estimated at approximately 740 million metric ton per year [1]. About 0.2 ton of RH is generated from every ton of rice produced [2], suggesting that about 148 million metric ton of RH is being generated annually. The generated RH has

very low commercial value and causes environmental issues pertaining to its disposal. RH is commonly discarded in the fields and used as fuel to generate steam for driving mechanical milling machinery in rice mills [3]. These activities could lead to the suspension of crystalline silica particles such as quartz and cristobalite in the air which causes silicosis disease [4]. In addition, the open burning of the RH leads to air pollution and endanger the motorists due to the deteriorating visibility. Therefore, conversion and utilization of the RH into useful materials are essential to solve the existing environmental and waste management problem, which in turn contributes to wealth generation for the rice producing nations.

RH comprises about 72 % of organic content (for example, cellulose, hemicelluloses and lignin), with the remaining composition made up of moisture content and ash [5, 6]. The content of each of these individual components depend on the rice variety, climatic conditions and geographical location of growth [7]. For instance, according to astudy by Govindarao (1980), RH samples obtained from two southern part of India (Trivandrum and Hyderabad) show relatively high Mg, Al and Fe content than the samples obtained from other countries. The presence of these elements is due to the use of chemical fertilizers in the paddy field [8]. These elements would affect the purity of rice husk ash (RHA) which used as a source for silica. The average percentage compositions of RH from different countries (dry basis) are cellulose 33.71 %, hemicellulose 23.14 %, lignin 19.30 %, ash 15.65 %, extractives 6.30 & and moisture 7.60 % (Table 1). RH, as a feedstock, could potentially be converted into adsorbents such as activated carbon (AC), zeolites as well as mesoporous silica via several processing methods [5]. The utilization and conversion of this biomass into low cost adsorbents is feasible since they are renewable sources, inexpensive and abundantly available [5, 9]. The conversion of RH into low cost adsorbents with excellent pore characteristics could overcome the byproducts and waste disposal problems while concurrently formulating value added products derived from RH.

Wee-Keat Cheah, Chee-Heong Ooi: School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia Enginee ring Campus, 14300 Nibong Tebal, Penang, Malaysia

^{*}Corresponding Author: Fei-Yee Yeoh: School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia Engineering Campus, 14300 Nibong Tebal, Penang, Malaysia, E-mail: feiyee@usm.my, Tel: +604-599 6175, Fax: +604-5941011

Table 1: Composition of rice husk from selected countries.

Constituents			Composition	(%)		
Constituents	Malaysia [10]	Thailand [11]	India [12]	India [13]	Taiwan [14]	Average
Cellulose	35.5	34.4	33	31.1	34.56	33.71
Hemicellulose	22.3	29.3	19.4	22.5	22.18	23.14
Lignin	13.6	19.2	14.5	22.3	26.91	19.30
Ash	16.1	17.1	20.6	13.9	10.54	15.65
Extractives	3.3	n.a	12.5	2.3	n.a	6.03
Moisture	9.1	n.a	n.a	7.9	5.81	7.60

The ash of RH contains about 87 to 97 wt % of silica in a hydrated amorphous form and other impurities [15] and thus could be utilized as precursor for the synthesis involving silicate sources. Study by Riveros and Garza (1986) reported that silica with purity up to 99.98 % could be obtained from RHA [16]. Moreover, RHA can also be used as alternative precursor for the preparation of active silica with high specific surface area [17]. According to studies conducted by Chen and co-workers, AC was successfully prepared from RH by using KOH, NaOH, Na₂CO₃ as well as K₂CO₃ as activating agents, through heat treatment at different temperatures [18]. RH-based AC with excellent pore characteristics (BET surface area up to 3014 m²g⁻¹ and total pore volume 1.78 cm³g⁻¹) was prepared by Guo and co-workers via KOH activation process [19]. The RH-based AC exhibited good Cr removal capacity (33.7 mgg^{-1}). Moreover, the AC derived from RH is also used as electrode materials for batteries and capacitors [20].

2 Preparation of activated carbon derived from rice husk

RH-derived AC is a porous carbonaceous solid material which exhibited large surface area and high porosity [21]. The highly porous structure of RH-derived AC enables it to adsorb substances from gas and liquid phases [22]. The pore characteristics and adsorption capability of the AC are influenced by the type of raw materials used and activation routes selected. AC is normally produced via carbonization and activation of the RH precursor. These processes are essential to develop a porous structure and increase the pore volume of RH-derived AC.

Carbonization process is typically carried out at temperatures ranging from 500 to 900°C, to eliminate the non-carbon elements found in RH such as nitrogen, oxygen,

hydrogen and nitrogen as volatile gaseous products [23]. The remnant carbon atoms would assemble into aromatic sheets (cross-linked in a random manner) and form free interstices which lead to the formation of pores. The pores created in carbonized RH would be further developed via activation process. Activation widens the existing pores by burning off the walls between adjacent pores and removing the disorganized carbon that block the pores in carbonized RH. Activation process could be applied through one of the three methods during the preparation of RH-derived AC, namely physical, chemical and physiochemical (combination of physical and chemical) activation [24].

2.1 Physical activation

Physical activation comprises the carbonization of RH to eliminate organic matters and followed by activation (two-steps process). The typical synthesis route for the preparation of RH-derived AC via physical and chemical activation is shown in Figure 1. The precursor RH is normally washed with de-ionized (DI) water to remove dust and attached particles, followed by drying process. The carbonization process is carried out at temperatures of 500 to 900 °C under the nitrogen or argon gas atmosphere and followed by subsequent activation. During the activation, the carbonized RH is gasified by CO₂, steam or their mixture at high temperature ranging from 800 to 1000 °C [25].

These activating agents eliminate carbon atoms from the carbonized RH as CO to ease the pores development [18]. The activation route using two different activating agents CO_2 and steam would result in AC with significantly porous structure and physical properties [26]. CO_2 activating agent creates pore openings, followed by the widening of narrow microporosity which eventually result in AC with larger micropore volume but narrower micropore size distribution [27]. Steam activating agent widens the micropores in biochar from the early stages of the ac-

tivation process and thus produces AC with a wider pore size distribution (micropores and mesopores) [28]. CO_2 is a preferable activating agent for activation process due to its inherent cleanliness and ease of handling. Moreover, CO_2 gas also facilitates in controlling the activation process due to the slow reaction rate at temperatures around $800\ ^{\circ}C$ [29].

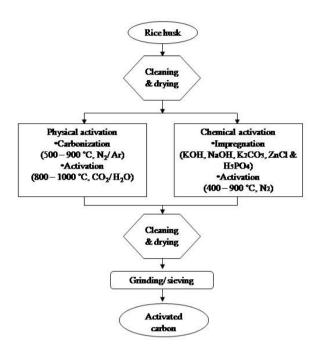


Figure 1: Physical and chemical activation for the preparation of AC derived from RH.

2.2 Chemical activation

Chemical activation of RH-derived AC involves both carbonization and activation being performed in a single step using chemical agents such as KOH, NaOH, $\rm H_3PO_4$ and $\rm ZnCl_2$ [18]. A cleaned RH is impregnated with activating agent in the form of concentrated solution to remove the cellulosic materials. The chemical impregnated RH precursor is then pyrolyzed at temperatures ranging from 400 to 900 °C in the absence of air [30]. The use of chemical activating agent inhibits the formation of tar and other byproducts (methanol and acetic acid), resulting in a better yield of RH-derived AC (above 30 wt %) [30]. The physical and chemical properties of the RH-derived AC are summarized in Table 2. This table presents two-steps (physical or physiochemical) activation and single-step activation conditions for the preparation of AC derived from RH.

The impregnation ratio between chemical activating agent and precursor is one of the major factor that greatly influences the yield and pore characteristics of RH-derived AC. Based on studies done by various researchers, the impregnation ratio (weight of chemical activating agent to weight of precursor) from 0.25 to 4 is normally applied on raw materials [31–33]. The yield of AC decreases when the impregnation increases. Large amounts of organic matter would be burnt off when more chemical activating agents are used to treat the precursors [31]. Studies by Angin (2013) and Kubota (2009) show that the increase in impregnation ratio resulted in better porosity development and widening of porous structure of the AC [31, 33]. Besides impregnation ratio, activation temperature is another factor which influences pore development, physical properties and yield of the AC. Activation at high temperatures could enhance the pores development of the RH-derived AC. Study by Guo and co-workers shows that the increase in activation temperature enhanced the pore characteristics of ACs derived from RH [19]. The increase in activation temperature from 650 to 800 °C increased the BET surface area (from 2110 to 3014 m^2g^{-1}) and micropore volume (from 0.14 to 0.44 cm 3 g $^{-1}$) of the RH-derived ACs.

For the preparation of RH-derived AC with good porosity, chemical activation offer several advantages over the physical activation. These advantages are single step activation process, higher yield obtained and better pores development in AC. A single step activation process could cut down on AC manufacturing time and energy required. Furthermore, the use of chemical activating agent could lower the activation temperature, shorten the activation time and enhance the porosity development in final RH-derived AC obtained [34]. However, there are certain drawbacks of using chemical activation for the RH-derived AC production. Additional cleaning step is required subsequent to the activation process to remove the residual chemicals. KOH and NaOH are hazardous, corrosive and expensive [35], while ZnCl₂ is unfriendly to the environment and creates waste disposal problem [36]. The use of chemical activating agents in treatment also increases the processing cost. Handling of the chemical activation agents might cause threat to health. Therefore, extra precautions are required to minimize the safety and health risk.

2.3 Biomedical adsorption applications of rice husk derived activated carbon

RH-based ACs play an important role in biomedical applications such as adsorption and purification of water, removal of dyes and hazardous gases. The RH-based ACs

 Table 2: Physiochemical properties of the activated carbon derived from rice husk.

	Activation	Chemical	BET surtace	Total pore	Purity of	Ash	Yield	Reference
temperature (°C)	temperature (°C)	treatment	area (m^2g^{-1})	volume (cm^3g^{-1})	carbon (%) CHN/S	content (%)	(%)	
Two-steps								
400	006	H_3PO_4	438.9	0.3871			37.69	[12]
200	800	КОН	3014	1.74				[19]
400	850	CO ₂	334	0.207	35	61.5	33.2	[37]
400	009	Steam	272.5			45.97		[38]
700		K_2CO_3 / microwave activation	1165	0.78		1.3	14.22	[39]
200	700	КОН	3263	1.772				[50]
400	006	КОН	2534	1.47				[40]
700	800	NaOH	1015	0.75				[41]
400	006	H_3PO_4	298.24	0.19825	48.97	41.84		[42]
200	800	КОН	1094.6	0.61				[43]
400	006	H_3PO_4	420		48.45		37.69	[44]
450	750	NaOH	2721	1.88				[45]
450	750	КОН	1930	0.97				[42]
Single-step								
	200	H_3PO_4			52.9		9.94	[46]
	009	ZnCl ₂	480		67.64			[47]
	006	КОН	3044	2.25				[48]
	200	H_3PO_4	1803	3.2		4.98	29.36	[49]
	200	$ZnCl_2$	2434	1.344	82.71	0.10	28	[14]
	200	H_3PO_4	1741	1.315	76.87	3.16	33	[14]
	650	КОН	280	0.206	44.3	42.6	33.4	[20]

with high surface areas and wide range of pore size are required to remove all type of adsorbates efficiently [12]. Adsorption is a process in which atoms or molecules in solid, liquid or gas phases attract onto the surface of RH-derived AC due to physical or chemical forces [51]. Table 3 shows the properties of RH-derived AC required for biomedical applications.

RH-derived AC is a potential medicine for the treatment of poisoning and drug overdoses. The RH-derived AC can be used to reduce bloating, lower cholesterol, treat bile flow problems safely during pregnancy and prevent hangovers [52, 53]. The RH contains fewer impurities compared to the conventional precursors such as coal, phenolic resin, acrylic fiber and polyacrylonitrile (PAN) [5]. All the impurities and organic matters in RH-derived AC is removed after going through the carbonization and activation processes, thus it is safe to be used as medicine. RH-derived AC prepared via physical activation method is preferable adsorbent for medicine due to the cleanliness and free of chemical. RH-derived AC with high surface area (more than $500 \, \text{m}^2 \text{g}^{-1}$) and adsorption capacity are essential for the rapid and complete removal of toxins and chemicals in the body [51, 54].

RH-derived AC have been widely used for the water purification and waste water treatment due to its excellent porosity and relatively high surface area [41, 50]. AC with BET surface area ranged from 400 to 1015 m² g⁻¹ can be prepared from RH via chemical activation process [41, 55, 56]. These porous RH-derived ACs are used in the removal contaminants such as rare earth elements (lanthanum and erbium) and heavy metals (Fe, Mn, Zn, Cu, Cd and Pb) from waste water (efficiency of adsorption is above 90 %). RH-derived AC prepared in the granular form is more preferable than the powdered RH-derived AC (RH ground into powder form prior to activation process) in water purification application. This is because the large particle size of granular RH-derived AC prevents the excessive pressure drop in the bed and avoids the carbon particles being carried away carry [57].

RH-based AC treated with ortho-phosphoric acid is used for enzyme (acid protease) immobilization in various biological and chemical systems due to its extensive applications in the fields of food and medicine [58, 59]. At optimized condition (pH 6), the acid protease adsorption capacity exhibits by RH-based AC exhibits is 150 mg g $^{-1}$. AC is a common adsorbent used in hemoperfusion since it was first introduced in 1963 to remove uremic toxins from patient's blood [60]. The initial trial of AC as adsorbent in hemoperfusion system showed poor hemocompatibility and released carbon particles into the blood stream lead to particle embolization, which is a serious clini-

cal side effect. Eventually a semi-permeable biocompatible polymeric coating was introduced to the AC and applied in hemoperfusion treatment. The membrane coating of AC prevents the release of carbon particles into blood stream and improved the hemocompatibility [61]. Thus, RH-derived AC with excellent pore characteristics could be applied in the hemoperfusion application by the introduction of semi-permeable biocompatible polymeric coating [62].

3 Silica derived from rice husk and rice husk ash

The approach of RH conversion into AC could further value-add this otherwise waste biomass. However, RH is conventionally fed (as-milled or packed into fuel blocks) to boilers for power generation through combustion process. Thus, aside from the organic RH biomass, rice husk ash (RHA) is continuously generated as a by-product from power generators serving the local on-site rice production industry. RHA could be used a source of silica since RHA is inherently silica-rich with composition >90.00 % [63].

According to Table 4, the composition of ash from the combustion of RH comprises of mainly silica. The most common use of siliceous RHA is in the construction materials industry, as an alternative raw material to conventional mined silica [64–66].

The silica composition found in RHA is mainly in the form of active silica [69, 70]. The active silica found in RHA possesses inherently high specific surface area and porosity to a certain extent [17]. Figure 2 shows the SEM micrograph of RHA after combustion at 750 °C for 6 h. A porous structure which would give high specific surface area could clearly be seen in the micrograph. According to the study reported by Liou (2004), nitrogen adsorption carried out on RHA reveals a narrow and bi-modal pore size distribution based on the Barrett-Joyner-Halenda (BJH) method (desorption) [71], with mode pore size of approximately 2.5 and 4.0 nm. The narrow pore size distribution of RHA, which falls in the mesoporous range, could be utilized to for various applications, particularly for applications involving adsorption. Several studies have been conducted with RHA as an adsorbent material for the liquid phase adsorption of lead, mercury [72, 73], phenol [74], cadmium, nickel [75] and lead [72, 76].

The application of siliceous RHA in cement and concrete as a pozzolanic material has been widely studied due to the high silica content and characteristic porosity [17, 77, 78]. According to ASTM C219-94, pozzolans are

Table 3: Properties of RH-derived AC required for biomedical applications.

Application	Properties and requirements		
Medicine for treatment of poisoning and	Biomass as precursor [5]		
drug overdoses	High surface area & adsorption capacity [51, 54]		
	Prepare via physical activation		
Water purification & waste water treatment	High surface area & pore volume [41, 50]		
	Rapid adsorption		
	Granular activated carbon [57]		
Enzyme immobilization	High surface area & pore volume		
	Treated with ortho-phosphoric acid [58, 59]		
Hemoperfusion	High surface area & pore volume [60]		
	Granular activated carbon		
	Coating of semipermeable synthetic membrane on the adsorbent [62]		

Table 4: Composition of RHA after heat treatment.

Components	Malaysia (%) [63]	Taiwan (%) [67]	Thailand (%) [68]	Brazil (%) [17]	Average (%)
expressed as oxides					
SiO ₂	92.00	95.60	92.80	94.95	93.84
Al_2O_3	0.18		0.11	0.39	0.23
Fe_2O_3	0.20	0.24	0.17	0.26	0.22
CaO	0.83	0.70	0.70	0.54	0.69
Na_2O	0.03		0.08	0.25	0.12
K ₂ O	1.70	2.66	3.35	0.94	2.16
MnO	0.06			0.16	0.11
TiO ₂		0.02		0.02	0.02
MgO	0.56			0.90	0.73
$P_{2}O_{5}$	0.77	0.52	1.07	0.74	0.78
SO ₃	0.39	0.15			
ZnO	0.02				
MgO			0.77		0.77
NiO	trace				
CuO	trace				
Rb2O	trace				
Sr0	trace				
Loss on ignition				0.85	

silica or alumina containing material which forms cementitious hydrates with calcium hydroxide at normal temperatures in the presence of moisture [79]. The displacement of Portland cement in cement and concrete compositions with RHA could effectively benefit the environment as Portland cement is conventionally mined as opposed to the agricultural waste RHA [80]. Additionally, the improvement in the cement and concrete physical properties with the addition of RHA as a pozzolan further solidifies the presence of RHA as essential additives in this industry [17, 77, 78].

3.1 Synthesis of mesoporous silica, silica xerogel and zeolite from rice husk ash

RHA or specifically the form of active silica could be further converted into bioactive porous materials mesoporous silica, silica xerogel and zeolite. Initially RHA is converted into precursor sodium silicate solution through a hydrothermal process. Further conversion of sodium silicate into mesoporous silica, silica xerogel and zeolite is as generalized in Figure 3.

Although raw RHA can be characterized as a material with high contents of mesoporous silica, the natu-

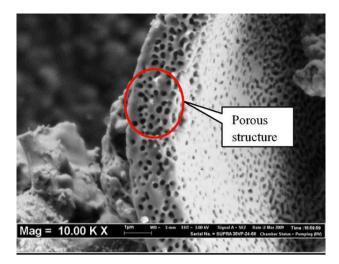


Figure 2: SEM micrograph of RHA after combustion at 750 °C for 6 h [63].

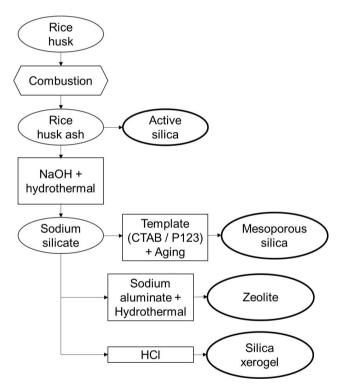


Figure 3: Preparation and synthesis of active silica, mesoporous silica, silica xerogel and zeolite from RH and RHA.

ral as-calcined RHA possesses lower porosity compared to synthesized mesoporous silica variants, for example SBA-15 [81], MCM-41 [82] and MCM-48 [83]. Following the combustion of RH, the RHA produced has to be washed repeatedly with distilled water to remove particles such as soil and dust from the ash, followed by a drying process. Subsequently, the cleaned RHA is converted into sodium silicate through heating and stirring of the RHA with sodium

hydroxide and distilled water. The resulting mixture is centrifuged to recover the solution, sodium silicate.

The major difference between the typical mesoporous silica synthesis and RHA-derived mesoporous silica is the conversion of RHA into sodium silicate precursor [81, 82]. The prepared sodium silicate is then used as silica source or precursor along with structure directing templates P123, CTAB and LE-4 for the synthesis of SBA-15, MCM-41 and MCM-48 respectively using a hydrothermal method. Table 5 below summarizes reagents and parameters used for the preparation of sodium silicate precursor and resulting mesoporous silica.

Aside from mesoporous silica, bioactive silica xerogel could also be derived from RHA through gel casting technique [87]. Silica is dissolved in NaOH to extract sodium silicate solution [88]. The pH of the extracted sodium silicate solution is then adjusted to pH 6 with the addition of HCl solution. The obtained gel is dried at 100 °C for 12 hours, resulting in silica xerogel.

Aside from the silica based porous materials, the introduction of sodium aluminate to the RHA extracted sodium silica results in the yield of zeolite. The composition of natural occurring zeolite is mainly aluminosilicate. Silicarich rice husk ash could be converted into sodium silicate and used as a precursor for the silicate constituent of zeolite. The conversion of rice husk ash into is closely similar to methods previously summarized in the prior section of mesoporous silica. Sodium hydroxide is mixed and stirred with cleaned RHA. The resulting mixture is centrifuged and the solution obtained is sodium silicate.

Zeolites NaA and NaY are synthesized through a seeding technique [63]. Both zeolites are similar in terms of structure, with an exception of difference in the number of member rings. NaA and NaY are synthesized through preparation of colloidal commercial sodium aluminate and RHA-derived sodium silicate at different molar ratios [63]. The seed gel was The calculated weight ratios (Al₂O3:10SiO₂) to the colloidal seed are subjected to hydrothermal treatment at 100 °C for 5 h [63]. XRD confirms the formation of zeolite NaA (Fig. 4) and zeolite NaY (Fig. 5). A variation in the aging duration, 24 h and 48 h resulted in zeolites with smaller particle size and hence higher surface area, as seen in Fig. 5 [89].

The preparation of feedstock gel was calculated based on a weight ratio to colloidal seed instead of molar ratio for a convenience of synthesis procedure. Next, the Teflon bottle was heated in an oven at 100 °C for 5 hours

Table 5: RHA-derived mesoporous silica synthesis conditions.

Sodium silicate synthesis conditions	Template	Aging conditions	Mesoporous silica	(Ref)
NaOH, 25/40/105 °C, 24 h	CTAB	145 °C, 36 h	MCM-41	[84]
2 M NaOH in H ₂ O at 70 °C for 24 h	CTAB	100°C, 72 h	MCM-41	[85]
2 M NaOH in H ₂ O at 70 °C for 24 h	CTAB, LE-4	100°C, 48 h	MCM-48	[85]
2 M NaOH in H ₂ O at 70 °C for 24 h	P123	40 °C, 24 h	SBA-15	[85]
NaOH, 2 h, 80 °C	CTAB, T-100	97°C, 38 h	MCM48 + 41	[86]
NaOH	P123, CTAB	100 °C, 24 h	SBA-15 + 3	[81]

Table 6: Properties of RHA-derived mesoporous biomaterials required for biomedical applications.

Application	Properties and requirements
Drug delivery	High surface area & pore volume
	Organic silica source
	Porosity for delayed drug release [93]
Water purification & waste water treatment	High surface area & pore volume
	Rapid adsorption
	Low cost [96]
Hemostatic agent	Water adsorption [94, 95]
	Rapid adsorption [94, 95]
	Zeolite [94, 95]
Bone scaffold	Interconnected pores [87, 97]
	Biocompatibility [87, 97]
	Silica xerogel [87, 97]

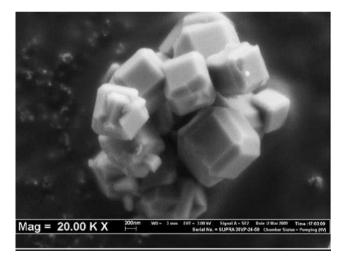


Figure 4: Zeolite NaA [63].

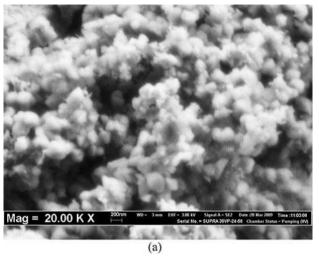
3.2 Biomedical applications of mesoporous silica, silica xerogel and zeolite from rice husk ash

The RHA precursor itself is porous in nature. RHA possesses a broad range pore size distribution and an approximate BET surface area of $36 \text{ m}^2/\text{g}$ [90]. The unconverted

RHA as a low cost adsorbent material typically for bulk adsorption application such as water purification. RHA has been reported to be able to effectively remove fluorides [91] and even heavy metals [92] from contaminated water sources. Aside from liquid phase adsorption, bulk RHA could be used for the adsorption of CO² [85].

The synthesis of various mesoporous silica (MCM-41, SBA-15) from sodium silicate extracted from RHA yields higher surface area compared to the original RHA or active silica. Jullaphan and co-workers reported that surface area of mesoporous silica synthesized using a mixture of CTAB and pluronics P123 could achieve a surface area of up to 955 m²/g [81]. This mesoporous structure could be exploited for drug delivery applications. Drugs loaded in the mesopores would gradually be released over a longer period of time compared to the burst release by non-porous carrier particles. RHA derived mesoporous silica has been used for the delivery of drugs such as ibuprofen and penicillin-G [93]. As with RH derived AC, the potential of RHA derived drug carriers for the current is huge due to the fact that the silica originates from an organic source.

The application of zeolites in the biomedical field is predominantly as a hemostatic agent. The efficient water



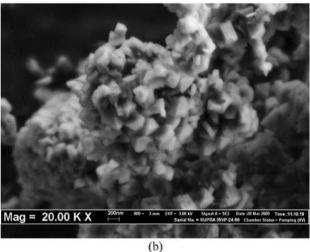


Figure 5: Zeolite NaY [63].

adsorption by zeolite effectively reduces the moisture content of an open wound thus triggering blot clot [94, 95]. However, the study on RHA derived zeolites for this particular biomedical application remains limited at the moment. Similar to the drug delivery using an organic silica source, the use of organic zeolites should be welcomed by the general public.

As for silica xerogel, the sintering of gel-casted RHA derived silica xerogel powder at different temperatures results in phase conversion. The sintering temperature of silica xerogel should be maintained below 1200 °C to prevent the transformation of amorphous silica phase into crystobalite [87]. The incubation of sintered silica xerogel scaffold in SBF solution showed the formation of hydroxylcarbonate apatite, a phase similar to that of the human bone.

Table 6 below summarizes the properties of RHAderived mesoporous biomaterials required for biomedical applications.

4 Conclusion

The conversion of rice husk biomass into value-added nanoporous adsorbent materials is equivalent to the conversion of waste to wealth. The conventional rice husk biomass disposal is through combustion for power generation. Subsequent reuse and reutilization of the RH biochar and RHA as a low cost precursor for the manufacturing of activated carbon, mesoporous silica and zeolite would effectively reduce the overall global carbon footprint using such zero carbon raw materials. The high silica purity of RHA makes it an ideal alternative silica source which requires minimal purification and extraction.

References

- Rice Market Monitor, in, Food and Agriculture Organization of the United Nations, 2014.
- [2] S. Kumagai, Y. Noguchi, Y. Kurimoto, K. Takeda, Oil adsorbent produced by the carbonization of rice husks, Waste management, 27 (2007) 554-561.
- [3] C. Sookkumnerd, N. Ito, K. Kito, Financial viabilities of husk-fueled steam engines as an energy-saving technology in Thai rice mills, Applied energy, 82 (2005) 64-80.
- [4] A.M. Yusof, N.A. Nizam, N.A.A. Rashid, Hydrothermal conversion of rice husk ash to faujasite-types and NaA-type of zeolites, Journal of Porous Materials, 17 (2010) 39-47.
- [5] S. Chandrasekhar, K. Satyanarayana, P. Pramada, P. Raghavan, T. Gupta, Review processing, properties and applications of reactive silica from rice husk—an overview, Journal of materials science, 38 (2003) 3159-3168.
- [6] N. Yalcin, V. Sevinc, Studies on silica obtained from rice husk, Ceramics International, 27 (2001) 219-224.
- [7] C. Deiana, D. Granados, R. Venturini, A. Amaya, M. Sergio, N. Tancredi, Activated carbons obtained from rice husk: influence of leaching on textural parameters, Industrial & Engineering Chemistry Research, 47 (2008) 4754-4757.
- [8] V. Govindarao, Utilization of rice husk-a preliminary-analysis, Journal of Scientific & Industrial Research (JSIR), 39 (1980) 495-515.
- [9] G. Crini, Non-conventional low-cost adsorbents for dye removal: A review, Bioresource Technology, 97 (2006) 1061-1085.
- [10] I. Rahman, J. Ismail, H. Osman, Effect of nitric acid digestion on organic materials and silica in rice husk, J. Mater. Chem., 7 (1997) 1505-1509.
- [11] P.T. Williams, N. Nugranad, Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks, Energy, 25 (2000) 493-513
- [12] L.J. Kennedy, J.J. Vijaya, G. Sekaran, Effect of two-stage process on the preparation and characterization of porous carbon composite from rice husk by phosphoric acid activation, Industrial & Engineering Chemistry Research, 43 (2004) 1832-1838.
- [13] P.S. Kumar, K. Ramakrishnan, S.D. Kirupha, S. Sivanesan, Thermodynamic and kinetic studies of cadmium adsorption from aqueous solution onto rice husk, Brazilian Journal of Chemical

- Engineering, 27 (2010) 347-355.
- [14] T.-H. Liou, S.-J. Wu, Characteristics of microporous/mesoporous carbons prepared from rice husk under base- and acid-treated conditions, Journal of Hazardous Materials, 171 (2009) 693-703.
- [15] J.M. Chen, F.W. Chang, The chlorination kinetics of rice husk, Industrial & Engineering Chemistry Research, 30 (1991) 2241-2247.
- [16] H. Riveros, C. Garza, Rice husks as a source of high purity silica, Journal of Crystal Growth, 75 (1986) 126-131.
- [17] V. Della, I. Kühn, D. Hotza, Rice husk ash as an alternate source for active silica production, Materials Letters, 57 (2002) 818-821.
- [18] Y. Chen, Y. Zhu, Z. Wang, Y. Li, L. Wang, L. Ding, X. Gao, Y. Ma, Y. Guo, Application studies of activated carbon derived from rice husks produced by chemical-thermal process—A review, Advances in colloid and interface science, 163 (2011) 39-52.
- [19] Y. Guo, J. Qi, S. Yang, K. Yu, Z. Wang, H. Xu, Adsorption of Cr (VI) on micro-and mesoporous rice husk-based active carbon, Materials Chemistry and Physics, 78 (2002) 132-137.
- [20] D. Liu, W. Zhang, H. Lin, Y. Li, H. Lu, Y. Wang, A green technology for the preparation of high capacitance rice husk-based activated carbon, Journal of Cleaner Production, (2015).
- [21] H. Marsh, F.R. Reinoso, Activated carbon, Elsevier, 2006.
- [22] H. Jankowska, A. Świątkowski, J. Choma, T.J. Kemp, Active carbon, Ellis Horwood New York, 1991.
- [23] W.M.A.W. Daud, W.S.W. Ali, M.Z. Sulaiman, The effects of carbonization temperature on pore development in palm-shellbased activated carbon, Carbon, 38 (2000) 1925-1932.
- [24] B.H. Hameed, A.T.M. Din, A.L. Ahmad, Adsorption of methylene blue onto bamboo-based activated carbon: Kinetics and equilibrium studies, Journal of Hazardous Materials, 141 (2007) 819-825.
- [25] K. Yang, J. Peng, H. Xia, L. Zhang, C. Srinivasakannan, S. Guo, Textural characteristics of activated carbon by single step CO2 activation from coconut shells, Journal of the Taiwan Institute of Chemical Engineers, 41 (2010) 367-372.
- [26] V. Gaur, A. Sharma, N. Verma, Preparation and characterization of ACF for the adsorption of BTX and SO 2, Chemical Engineering and Processing: Process Intensification, 45 (2006) 1-13.
- [27] N. Cao, H. Darmstadt, F. Soutric, C. Roy, Thermogravimetric study on the steam activation of charcoals obtained by vacuum and atmospheric pyrolysis of softwood bark residues, Carbon, 40 (2002) 471-479.
- [28] F. Rodriguez-Reinoso, M. Molina-Sabio, M. González, The use of steam and CO2 as activating agents in the preparation of activated carbons, Carbon, 33 (1995) 15-23.
- [29] R.C. Bansal, M. Goyal, Activated Carbon Adsorption, Taylor & Francis Group, (2005) 1-469.
- [30] R.C. Bansal, J.-B. Donnet, F. Stoeckli, Active carbon, M. Dekker, 1988
- [31] D. Angın, E. Altintig, T.E. Köse, Influence of process parameters on the surface and chemical properties of activated carbon obtained from biochar by chemical activation, Bioresource Technology, 148 (2013) 542-549.
- [32] D. Kalderis, S. Bethanis, P. Paraskeva, E. Diamadopoulos, Production of activated carbon from bagasse and rice husk by a single-stage chemical activation method at low retention times, Bioresource Technology, 99 (2008) 6809-6816.
- [33] M. Kubota, A. Hata, H. Matsuda, Preparation of activated carbon from phenolic resin by KOH chemical activation under mi-

- crowave heating, Carbon, 47 (2009) 2805-2811.
- [34] Ö. Gerçel, A. Özcan, A.S. Özcan, H.F. Gercel, Preparation of activated carbon from a renewable bio-plant of Euphorbia rigida by H 2 SO 4 activation and its adsorption behavior in aqueous solutions, Applied Surface Science, 253 (2007) 4843-4852.
- [35] M. Lillo-Ródenas, J. Marco-Lozar, D. Cazorla-Amorós, A. Linares-Solano, Activated carbons prepared by pyrolysis of mixtures of carbon precursor/alkaline hydroxide, Journal of Analytical and Applied Pyrolysis, 80 (2007) 166-174.
- [36] J. Guo, A.C. Lua, Textural and chemical characterisations of activated carbon prepared from oil-palm stone with H2SO4 and KOH impregnation, Microporous and Mesoporous Materials, 32 (1999) 111-117.
- [37] S. Kumagai, Y. Shimizu, Y. Toida, Y. Enda, Removal of dibenzothiophenes in kerosene by adsorption on rice husk activated carbon, Fuel, 88 (2009) 1975-1982.
- [38] P.K. Malik, Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow 36, Dyes and Pigments, 56 (2003) 239-249.
- [39] K. Foo, B. Hameed, Utilization of rice husks as a feedstock for preparation of activated carbon by microwave induced KOH and K2CO3 activation, Bioresource Technology, 102 (2011) 9814-9817.
- [40] D.-H. Jeon, T.-J. Lim, S.-J. Park, Role of microporosity of carbon produced from rice husks on electrochemical performance of Pt-Ru catalyst for direct methanol fuel cells, Journal of Industrial and Engineering Chemistry, 31 (2015) 244-250.
- [41] L. Lin, S.-R. Zhai, Z.-Y. Xiao, Y. Song, Q.-D. An, X.-W. Song, Dye adsorption of mesoporous activated carbons produced from NaOH-pretreated rice husks, Bioresource Technology, 136 (2013) 437-443.
- [42] S. Somasundaram, K. Sekar, V.K. Gupta, S. Ganesan, Synthesis and characterization of mesoporous activated carbon from rice husk for adsorption of glycine from alcohol-aqueous mixture, Journal of Molecular Liquids, 177 (2013) 416-425.
- [43] G. Wang, D. Wang, S. Kuang, W. Xing, S. Zhuo, Hierarchical porous carbon derived from rice husk as a low-cost counter electrode of dye-sensitized solar cells, Renewable Energy, 63 (2014) 708-714.
- [44] L.J. Kennedy, G. Sekaran, Integrated biological and catalytic oxidation of organics/inorganics in tannery wastewater by rice husk based mesoporous activated carbon—Bacillus sp, Carbon, 42 (2004) 2399-2407.
- [45] Y. Guo, J. Zhao, H. Zhang, S. Yang, J. Qi, Z. Wang, H. Xu, Use of rice husk-based porous carbon for adsorption of Rhodamine B from aqueous solutions, Dyes and Pigments, 66 (2005) 123-128.
- [46] I. Rahman, B. Saad, S. Shaidan, E.S. Rizal, Adsorption characteristics of malachite green on activated carbon derived from rice husks produced by chemical-thermal process, Bioresource Technology, 96 (2005) 1578-1583.
- [47] N. Yalçın, V. Sevinc, Studies of the surface area and porosity of activated carbons prepared from rice husks, Carbon, 38 (2000) 1943-1945.
- [48] Y.-J. Heo, S.-J. Park, Synthesis of activated carbon derived from rice husks for improving hydrogen storage capacity, Journal of Industrial and Engineering Chemistry, 31 (2015) 330-334.
- [49] L. Ding, B. Zou, L. Shen, C. Zhao, Z. Wang, Y. Guo, X. Wang, Y. Liu, A simple route for consecutive production of activated carbon and liquid compound fertilizer from rice husk, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 446 (2014)

- 90-96.
- [50] A. Daifullah, B. Girgis, H. Gad, Utilization of agro-residues (rice husk) in small waste water treatment plans, Materials Letters, 57 (2003) 1723-1731.
- [51] R.C. Bansal, M. Goyal, Activated carbon adsorption, CRC press, 2010.
- [52] Activated Charcoal, in: Vitamins & Supplements, 2016.
- [53] T. Albertson, R.W. Derlet, G.E. Foulke, M. Minguillon, S. Tharratt, Superiority of activated charcoal alone compared with ipecac and activated charcoal in the treatment of acute toxic ingestions, Annals of emergency medicine, 18 (1989) 56-59.
- [54] C. Ronco, L. Fecondini, The Vicenza wearable artificial kidney for peritoneal dialysis (ViWAK PD), Blood purification, 25 (2007) 383-388.
- [55] N. Awwad, H. Gad, M. Ahmad, H. Aly, Sorption of lanthanum and erbium from aqueous solution by activated carbon prepared from rice husk, Colloids and Surfaces B: Biointerfaces, 81 (2010) 593-599.
- [56] Y. Liu, Y. Guo, Y. Zhu, D. An, W. Gao, Z. Wang, Y. Ma, Z. Wang, A sustainable route for the preparation of activated carbon and silica from rice husk ash, Journal of Hazardous Materials, 186 (2011) 1314-1319.
- [57] T.J. Bandosz, Activated Carbon Surfaces in Environmental Remendiation, 2006.
- [58] A.G. Kumar, S. Swarnalatha, P. Kamatchi, G. Sekaran, Immobilization of high catalytic acid protease on functionalized mesoporous activated carbon particles, Biochemical Engineering Journal, 43 (2009) 185-190.
- [59] J. Hu, S. Li, B. Liu, Properties of immobilized pepsin on modified PMMA microspheres, Biotechnology journal, 1 (2006) 75-79.
- [60] H. Yatsidis, A convenient hemoperfusion microapparatus over charcoal for the treatment of endogenous and exogenous intoxications. Its use as an effective artificial kidney, in: Proc. European Dialysis Transplant Assoc, 1964, pp. 83.
- [61] S. Rosiński, D. Lewińska, W. Piątkiewicz, Application of mass transfer coefficient approach for ranking of active carbons designed for hemoperfusion, Carbon, 42 (2004) 2139-2146.
- [62] C. Howell, S. Sandeman, Y. Zheng, S. Mikhalovsky, V. Nikolaev, L. Sakhno, E. Snezhkova, New dextran coated activated carbons for medical use, Carbon, 97 (2016) 134-146.
- [63] W.-C. Tan, S.-Y. Yap, A. Matsumoto, R. Othman, F.-Y. Yeoh, Synthesis and characterization of zeolites NaA and NaY from rice husk ash, Adsorption, 17 (2011) 863-868.
- [64] E. Basha, R. Hashim, H. Mahmud, A. Muntohar, Stabilization of residual soil with rice husk ash and cement, Construction and Building Materials, 19 (2005) 448-453.
- [65] K. Ganesan, K. Rajagopal, K. Thangavel, Rice husk ash blended cement: assessment of optimal level of replacement for strength and permeability properties of concrete, Construction and Building Materials, 22 (2008) 1675-1683.
- [66] G. Habeeb, M. Fayyadh, Rice husk ash concrete: the effect of RHA average particle size on mechanical properties and drying shrinkage, Australian Journal of Basic and Applied Sciences, 3 (2009) 1616-1622.
- [67] C.-L. Hwang, T.-P. Huynh, Effect of alkali-activator and rice husk ash content on strength development of fly ash and residual rice husk ash-based geopolymers, Construction and Building Materials, 101 (2015) 1-9.
- [68] K. Kunchariyakun, S. Asavapisit, K. Sombatsompop, Properties of autoclaved aerated concrete incorporating rice husk ash as

- partial replacement for fine aggregate, Cement and Concrete Composites, 55 (2015) 11-16.
- [69] C. Prasad, K.N. Maiti, R. Venugopal, Effect of rice husk ash in whiteware compositions, Ceramics International, 27 (2001) 629-635.
- [70] C. Prasad, K.N. Maiti, R. Venugopal, Effect of substitution of quartz by rice husk ash and silica fume on the properties of whiteware compositions, Ceramics International, 29 (2003) 907-914.
- [71] T.-H. Liou, Preparation and characterization of nano-structured silica from rice husk, Materials Science and Engineering: A, 364 (2004) 313-323.
- [72] Q. Feng, Q. Lin, F. Gong, S. Sugita, M. Shoya, Adsorption of lead and mercury by rice husk ash, Journal of Colloid and Interface Science, 278 (2004) 1-8.
- [73] D. Tiwari, D. Singh, D. Saksena, Hg (II) adsorption from aqueous solutions using rice-husk ash, Journal of Environmental Engineering, 121 (1995) 479-481.
- [74] A. Mahvi, A. Maleki, A. Eslami, Potential of rice husk and rice husk ash for phenol removal in aqueous systems, (2004).
- [75] V.C. Srivastava, I.D. Mall, I.M. Mishra, Competitive adsorption of cadmium (II) and nickel (II) metal ions from aqueous solution onto rice husk ash, Chemical Engineering and Processing: Process Intensification, 48 (2009) 370-379.
- [76] T.K. Naiya, A.K. Bhattacharya, S. Mandal, S.K. Das, The sorption of lead (II) ions on rice husk ash, Journal of Hazardous Materials, 163 (2009) 1254-1264.
- [77] C. Rößler, D.-D. Bui, H.-M. Ludwig, Pozzolanic reactivity of mesoporous amorphous rice husk ash in portlandite solution, Construction and Building Materials, 59 (2014) 111-119.
- [78] C. Rößler, D.-D. Bui, H.-M. Ludwig, Rice husk ash as both pozzolanic admixture and internal curing agent in ultra-high performance concrete, Cement and Concrete Composites, 53 (2014) 270-278.
- [79] I. Odler, Special inorganic cements, CRC Press, 2003.
- [80] M. Nehdi, J. Duquette, A. El Damatty, Performance of rice husk ash produced using a new technology as a mineral admixture in concrete, Cement and concrete research, 33 (2003) 1203-1210.
- [81] O. Jullaphan, T. Witoon, M. Chareonpanich, Synthesis of mixedphase uniformly infiltrated SBA-3-like in SBA-15 bimodal mesoporous silica from rice husk ash, Materials Letters, 63 (2009) 1303-1306.
- [82] M. Bhagiyalakshmi, L.J. Yun, R. Anuradha, H.T. Jang, Synthesis of chloropropylamine grafted mesoporous MCM-41, MCM-48 and SBA-15 from rice husk ash: their application to CO2 chemisorption, Journal of Porous Materials, 17 (2010) 475-484.
- [83] H.T. Jang, Y. Park, Y.S. Ko, J.Y. Lee, B. Margandan, Highly siliceous MCM-48 from rice husk ash for CO 2 adsorption, International Journal of Greenhouse Gas Control, 3 (2009) 545-549.
- [84] W. Zeng, H. Bai, Swelling-agent-free synthesis of rice husk derived silica materials with large mesopores for efficient CO 2 capture, Chemical Engineering Journal, 251 (2014) 1-9.
- [85] M. Bhagiyalakshmi, L.J. Yun, R. Anuradha, H.T. Jang, 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, Journal of Hazardous Materials, 175 (2010) 928-938
- [86] H. Nur, L.C. Guan, S. Endud, H. Hamdan, Quantitative measurement of a mixture of mesophases cubic MCM-48 and hexagonal MCM-41 by 13 C CP/MAS NMR, Materials Letters, 58 (2004)

1971-1974.

- [87] J.P. Nayak, J. Bera, Bioactive Porous Silica Ceramics Prepared Using Rice Husk Ash by Gelcasting Method, in: Advanced Materials Research, Trans Tech Publ, 2012, pp. 12-16.
- [88] J. Nayak, J. Bera, Effect of sintering temperature on phaseformation behavior and mechanical properties of silica ceramics prepared from rice husk ash, Phase Transitions, 82 (2009) 879-888.
- [89] R. Mohamed, I. Mkhalid, M. Barakat, Rice husk ash as a renewable source for the production of zeolite NaY and its characterization, Arabian Journal of Chemistry, (2012).
- [90] V.C. Srivastava, I.D. Mall, I.M. Mishra, Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA, Journal of Hazardous Materials, 134 (2006) 257-267.
- [91] V. Ganvir, K. Das, Removal of fluoride from drinking water using aluminum hydroxide coated rice husk ash, Journal of hazardous materials, 185 (2011) 1287-1294.
- [92] L. Benassi, F. Franchi, D. Catina, F. Cioffi, N. Rodella, L. Borgese, M. Pasquali, L.E. Depero, E. Bontempi, Rice Husk Ash to Stabilize Heavy Metals Contained in Municipal Solid Waste Incineration Fly Ash: First Results by Applying New Pre-treatment Technology, Materials, 8 (2015) 6868-6879.
- [93] M. Salavati-Niasari, J. Javidi, M. Dadkhah, Ball milling synthesis of silica nanoparticle from rice husk ash for drug delivery application, Combinatorial chemistry & high throughput screening, 16 (2013) 458-462.
- [94] H.B. Alam, Z. Chen, A. Jaskille, R.I.L.C. Querol, E. Koustova, R. Inocencio, R. Conran, A. Seufert, N. Ariaban, K. Toruno, Application of a zeolite hemostatic agent achieves 100% survival in a lethal model of complex groin injury in swine, Journal of Trauma and Acute Care Surgery, 56 (2004) 974-983.
- [95] N. Ahuja, T.A. Ostomel, P. Rhee, G.D. Stucky, R. Conran, Z. Chen, G.A. Al-Mubarak, G. Velmahos, H.B. Alam, Testing of modified zeolite hemostatic dressings in a large animal model of lethal groin injury, Journal of Trauma and Acute Care Surgery, 61 (2006) 1312-1320.
- [96] P. Sharma, H. Kaur, M. Sharma, V. Sahore, A review on applicability of naturally available adsorbents for the removal of hazardous dyes from aqueous waste, Environmental monitoring and assessment, 183 (2011) 151-195.
- [97] A.A. Alshatwi, J. Athinarayanan, V.S. Periasamy, Biocompatibility assessment of rice husk-derived biogenic silica nanoparticles for biomedical applications, Materials Science and Engineering: C, 47 (2015) 8-16.



Fei-Yee YEOH

Fei-Yee YEOH is a director of Industry Network at Division of Industry and Community Network in Universiti Sains Malaysia (USM). He is also a senior lecturer at the School of Materials & Mineral Resources Engineering. He completed his master study in Materials Engineering, USM in 2004 with a special scholarship scheme. Fei-Yee was awarded an AUN/Seed-Net Scholarship by Japan International Cooperation Agency (JICA) for his doctoral research in Functional Materials Engineering at Toyohashi University of Technology, Japan. Prior to his academic career as a faculty member, he has also been a R&D engineer in a multinational company industry. Between 2015-2016, he was appointed by the Ministry of Higher Education (MOHE) to carry out a postdoctoral research in IBM. Other than being an author for a number of research papers and books, and holders of several intellectual properties, he is also a strategy planning consultant for MOHE, and a technology consultant to a number of industries. Each year, he has been awarded with numerous international visiting scientist and professorship, as well as national/international grants and awards from international exhibition. In 2014 and 2015 respectively, his nanoporous material project won the Global Cleantech Innovation Programme (GCIP) organized by United Nations Industry Development Organization (UNIDO) and was invited to San Francisco for the global awards in 2015. He actively participates in local and international professional organizations and their activities such as International Adsorption Society, Chemical Society of Japan, Board of Engineers Malaysia, Institute of Materials Malaysia and so forth. His current research interests focus on nanoporous biomaterials and bio-based materials for environment and biomedical applications.