REVIEW ARTICLE



Biochar from pyrolysis of rice husk biomass—characteristics, modification and environmental application

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Abstract

Biochar produced from various biomass has been widely used in environmental applications owing to its ability to immobilize or remove the contaminants from soil, water and air. The present work summarizes various pyrolysis variants used for biochar production from rice husk, modification of biochar and its environmental application. The high volatile matter content (70.2–78.5%) and carbon content (35.2–44.7%) favoured production of biochar from rice husk through pyrolysis. Microwave-assisted hydrothermal carbonization showed highest biochar yield from rice husk (57.9%) compared to other process variants, whereas wet pyrolysis produced biochar with the highest carbon content (71.2%). Steam activation of rice husk biochar resulted in a broader pore size distribution with the presence of significant micropores compared to CO_2 activation. A substantial improvement in surface area and microporous volume was observed with alkali activation compared to that of acid activation, whereas metal impregnation caused a reduction in surface area. Rice husk biochar with/without modification has been employed for adsorption of pollutants such as cations, dyes, nutrients and tetracycline. The nutrient-loaded rice husk biochar improved the soil fertility and cation exchange capacity. The studies indicated that the choice of suitable pyrolysis variant and biochar modification method is vital to improve the adsorption capacity and nutrient release potential of the rice husk biochar.

Keywords Rice husk biochar · Pyrolysis · Modification · Adsorption · Soil amendment

1 Introduction

Rice husk is the by-product of rice processing and is one of the plentiful resources in Asian countries [1]. India ranks second in global rice production, with 20–22% of the 122 million tons of world's rice production [2]. Rice husk management involves direct dumping into the soil, composting or burning them out in mass as a fuel [3]. However, composting was found to be ineffective due to low nitrogen content, whereas

Highlights for review

burning would give rise to the generation of a significant amount of fine particles into the air [4]. Therefore, safe disposing of the rice husk biomass is highly desired.

New practices of biomass management involve several wastes to energy conversion techniques through biochemical or thermochemical routes. The high carbon content in biomass such as rice husk facilitates its conversion into energy-rich biochar upon thermochemical treatment [5]. Among the thermochemical processes adopted, pyrolysis has received much attention in recent years due to its flexibility in both operating condition and the type of feedstock. Pyrolysis involves thermal degradation of biomass at elevated temperature in an oxygen-free atmosphere to obtain value-added by-products such as biochar, bio-oil and non-condensable gas. The quality of by-products, along with the reduction in greenhouse gas emission, makes the method superior to other technologies [6]. Outcomes from previous studies indicated that pyrolysis of rice husk biomass to biochar is an effective method both for biomass disposal and energy recovery [3, 7-12]. The present review summarizes the effects of pyrolysis process variants used for conversion of rice husk

Application of different pyrolysis variants for biochar production from rice husk

Yield and characteristics of rice husk biochar from different process variants

[·] Modifications of rice husk biochar to improve surface properties

[•] Environmental applications of as-received and modified rice husk biochar

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biomass on the yield and quality of biochar. Further various modifications adopted for enhancing the properties of biochar to be applied as an asset for environmental beneficiation are discussed.

2 Characteristics of rice husk biomass

Biomass is composed of lignin, cellulose and hemicellulose. The cellulose and lignin content in the biomass was one of the essential factors to assess the pyrolysis characteristics. Also, the relative composition of these constituents in biomass influenced the nature of the pyrolysis by-products. Studies revealed that both lignin and cellulose enhanced the biochar yield during pyrolysis. Pyrolysis of biomass with high lignin content resulted in higher biochar content compared to the one with lower lignin content due to the breakdown of relatively weak bonds and consequent formation of the solid structure [13, 14]. Rice husk biomass consists of various proportions of moisture content (MC), volatile matter content (VM), ash content (Ash) and fixed carbon content (FC) depending on its growth condition and geographic location. The reported range of MC, VM, Ash and FC in rice husk is 4.5-10.8%, 70.2-78.5%, 3.4-17% and 3.4-19.8% respectively (Table 1). The high VM, along with low ash and FC content, indicated possible thermal decomposition of rice husk [3].

On the other hand, ultimate analysis showed variation in elemental composition, viz. carbon, hydrogen, oxygen, nitrogen and sulphur (Table 1). High carbon content (35.2–44.7%) favoured the biomass in the production of higher biochar yield. Also, lower nitrogen content (0.2–1.6%) reduced the unfavourable situation for biomass pyrolysis that would lead to the release of toxic GHGs like NOx [15].

3 Pyrolysis process variants for biochar production

Several processes of pyrolysis have been employed for converting biomass into biochar. It is highly crucial to choose the appropriate method to obtain the maximum yield of the desired by-product in pyrolysis. All the process variants are carried out in an oxygen-free atmosphere that results in a reduction of greenhouse gas emission by biomass combustion [15]. Various process variants of pyrolysis based on the heating rate and mode of heating include wet pyrolysis, pyrolysis, torrefaction, slow pyrolysis, fast pyrolysis, flash pyrolysis, and microwave-assisted pyrolysis.

3.1 Wet pyrolysis

Wet pyrolysis or hydrothermal carbonization is a type of thermochemical conversion process for conversion of biomass into a coal-like product hydrochar or hydrothermal biochar. In wet pyrolysis, the feedstock with high moisture content up to 75–90% is subjected to pyrolysis in a pressurized vessel without any pre-drying step. The elevated temperature of \sim 180–250 °C along with high moisture content resulted in dehydration and decarboxylation of biomass constituents and its conversion into carbon-densified product [16]. The process resulted in partial carbonization of biomass to yield biochar with a high concentration of oxygen-containing functional groups and comparatively low H/C, and O/C ratio [17].

3.2 Pyrolysis

Biomass pyrolysis process incorporates thermal degradation of biomass that starts at 350-550 °C and goes up to 700-800 °C. The products obtained from this process include biochar, bio-oil and non-condensable gases such as methane, hydrogen, carbon monoxide and carbon dioxide. Higher moisture waste streams such as sludge and meat processing wastes are pretreated before the pyrolysis to reduce moisture content [6, 16]. In contrast, rice husk biomass, with low moisture content, can be pyrolyzed directly. During the process, more stable byproducts are obtained owing to the heating of biomass above its thermal stability limit in an inert atmosphere. Besides, the volatiles produced in the process could be condensed to retrieve bio-oil. Pyrolysis occurs in two stages. Biomass gets cleaved up and devolatilized in the first stage. Biomass gets converted to its main components, viz. lignin, cellulose and hemicellulose by cleavage along with the formation of carboxyl, carbonyl and hydroxyl groups [18]. The process of devolatilization results in decarboxylation, dehydration and dehydrogenation of the biomass. The second stage corresponds to the conversion of larger molecules/heavy compounds in biomass, leading to the formation of biochar, biooil or non-condensable gases. The second stage of the process can be accelerated by improving heating rate with the use of a catalyst [19, 20].

3.3 Torrefaction

Torrefaction process is carried out at low pyrolysis temperature of ~ 200–300 °C. In this method, the feed materials are heated up slowly at a heating rate of \leq 60 °C/min for hours to days [10]. The moisture content and volatiles from biomass are released at a slow rate, thus maintaining the rigid structure carbonaceous biomass. The process results in the partial decomposition of cellulose, hemicellulose and lignin. It tends to yield a higher proportion of solids compared to liquid and non-condensable gases. The solid obtained has high O/C ratio and hence cannot be referred as biochar [21]. Therefore, torrefaction is considered a pretreatment for moisture removal and densification of biomass to increase the heating value [15, 22].

Table 1 Characteristics of rice	husk biochar obtained from diffe	rent process	variants							
Process variants	Reactor	Operating	g conditio	ns	Biochar yield	Proximate ana	ılysis (%)	Ultimate anal	lysis (%)	References
		Temp (°C)	RT (h)	HR (°C/min)	(%)	Rice husk	Biochar	Rice husk	Biochar	
Wet pyrolysis	Autoclave reactor	220	-		32.9	MC, 4.5 VM, 78.5 Ash, 3.4 EC 12.4	MC, 2.9 VM, 55 Ash, 3.1 EC 20	C, 44.7 H, 6.2 O, 37.7 N 1.6	C, 66.3 H, 5 O, 26.4 N 2 2	[7]
		280	1		27.4		MC, 3.1 MC, 3.1 VM, 50.8 Ash, 2.5 FC, 42.6		C, 71.2 C, 71.2 H, 5 O, 21.3 N, 2.6	
Pyrolysis	Tube type reactor	350	1	15	40.10	MC, 4.5 VM, 78.5 Ash, 3.4 FC 13.4	MC, 6.1 VM, 28.3 Ash, 25.9 FC 39.7	C, 44.7 H, 6.2 O, 37.7 N 1 6	C, 55 H, 2.8 O, 41.2 N 0.8	[7]
		500	1	15	37.0		MC, 4.7 MC, 4.7 VM, 14.2 Ash, 33.7 FC, 47.4		N, 0.0 C, 58.2 H, 1.7 O, 39.2 N, 0.7	
Flash pyrolysis	Conical spouted bed reactor	800	1	15	26.0	VM, 70.5 Ash, 12.9 FC, 16.6	VM, 12.8 Ash, 51.3 FC, 36	C, 42 H, 5.4 O, 39.3 N 0.7	C, 45.2 H, 1.5 O, 1.7 N 0.7	[8]
Slow pyrolysis	Fixed bed reactor made of metallic cylinder	500	7	10	33.3		MC, 2.22 VM, 31.8 Ash, 20.04 FC 45 94			[33]
Fast pyrolysis	Fluidized bed induction heating system Nitrogen flow rate. 601 /min	550				MC, 10.08 VM, 72.40 Ash, 14.1 FC, 3.4	MC, 2.6 MM, 13.1 Ash, 50.9 FC, 33.4	C, 35.2 H, 4.2 O, 46.2 N, 0.36	C, 50.9 H, 1.83 O, 9.27 N. 0.3	[6]
Microwave-assisted hydrothermal carbonization	Microwave digester	180	0.34		57.9	MC, 8.53 VM, 70.20 Ash, 6.9 FC, 14.37	MC, 2.5 VM, 45.6 Ash, 16.5 FC, 35.4	C, 37.19 H, 4.8 O, 57.6 N 0.2	C, 48.8 C, 48.8 H, 5.0 O, 45.3 N, 04	[1]
Microwave-assisted pyrolysis	Microwave oven reactor Nitrogen flow rate, 0.2 L/min	600	0.25			MC, 9.18 MC, 9.18 VM, 78.2 Ash, 17 FC, 4.8			C, 59.6 O, 40.4	[3]
Torrefaction	Quartz reactor with thermal insulation coat Nitrogen flow rate, 0.5 L/min	230	0.5			VM, 64.89 Ash, 15.28 FC, 19.83	MC, 5.2 VM, 60.78 Ash, 16.2 FC, 23.03	C, 42.13 H, 5.4 O, 36.5 N, 0.55 S, 0.17	C, 42.4 H, 5.33 O, 36.5 N, 0.57 S, 0.18	[10]

Process variants	Reactor	Operating	conditions	Biochar yield	Proximate an	alysis (%)	Ultimate anal	ysis (%)	References
		Temp (°C)	RT HR (h) (°C/min)	(o_{λ})	Rice husk	Biochar	Rice husk	Biochar	
		290	0.5			MC, 1.4		C, 50.75	
						VM, 40.06		H, 4.32	
						Ash, 22.3		0, 22.4	
						FC, 37.68		N, 0.76	
								S, 0.18	

3.4 Slow and fast pyrolysis

Slow pyrolysis is generally carried out at a temperature of ~ 400–500 °C and heating rate (HR) of 0.1–1 °C/s that tends to increase the char yield along with the generation of thick biooil like tar [15, 21]. The slow heating rate necessitates the long process time of 5–30 min to complete the process. On the other hand, fast pyrolysis employs heating of the biomass to 400–650 °C at high HR of ~ 10-200 °C/s and for a period of 1–10 s. This process resulted in highest bio-oil yield (~ 60–70%), compared to biochar (15–20%) and syngas (10–20%) [6, 9].

3.5 Flash pyrolysis

Flash pyrolysis or ultrafast pyrolysis is likely to be carried out at a temperature range of 800–1000 °C obtained with HR \geq 1000 °C/s [23–26]. The biomass feed is converted to fine particles of < 0.2 mm prior to the pyrolysis process [21]. The flash process yields lesser amount of biochar compared to other by-products (Ibrahim et al., 2012). The biggest challenge of this method is to configure the reactor in which the input biomass can reside for a short amount of time under extremely high temperature and HR, which limits its industrial application [15]. Further, the stability and quality of the bio-oil, the major byproduct of the process, is strongly affected by the char content. Char present in the bio-oil can catalyze the polymerization reaction inside the liquid product which in turn causes an increase in the viscosity of oil [12, 27].

3.6 Microwave-assisted pyrolysis

In the conventional heating process, the heat transfer to the material occurs through conduction, convection and radiation, which limits its flexibility in maintaining control over the temperature, whereas microwave-assisted pyrolysis employs microwave radiation for heating that involves selective and volumetric heating of the biomass [3, 28–30]. During microwave heating, electromagnetic field enters the material, and it generates thermal energy throughout the penetration depth by dielectric heating due to interaction with dipoles present in the material, which results in volumetric heating from inside. Microwave heating generally requires a material with a high dielectric constant. Microwave absorbers are used along with the biomass to facilitate dielectric heating during the process. Microwave-assisted pyrolysis is conducted at a temperature of 400-800 °C, and it is considered an advancement over the conventional pyrolysis process [3, 16, 31]

4 Characteristics of rice husk biochar obtained from process variants

The properties of rice husk biochar obtained through various pyrolysis variants are listed in Table 1. The results depicted that the yield of biochars produced from wet pyrolysis and pyrolysis process showed a slight reduction from 37.9% to 27.4% and 40.1 to 37% with the rise in temperature from 220 to 280 °C and 350 to 800 °C respectively. This could due to the intensified degradation reaction such as decarboxylation, dehydration and aromatization at higher temperature that resulted in enhanced carbonization [7]. The wet pyrolysis of rice husk indicated a decrease in biochar yield compared to pyrolysis (Table 1). The low biochar yield in wet pyrolysis could be due to reduced degradation of cellulose, hemicellulose and lignin content [32]. The VM and ash content of biochar obtained from wet pyrolysis was high (~ 50%) compared to pyrolysis (~ 14%), indicating partial valorization of biomass in wet pyrolysis (Table 1). Conversely, the lower ash content in the biochar from wet pyrolysis process may be attributed to the higher amount of inorganic compound present in the supercritical water [7].

Slow pyrolysis of rice husk biomass showed that low temperature and longer vapour residence time favoured repolymerization of rice husk constituents by giving them sufficient time to react and thus improved biochar production [15], whereas high HR during flash pyrolysis of rice husk enhanced the de-polymerization of biomass into volatile primary components, which in turn, retarded biochar yield and improved bio-oil yield [8]. Also, the less retention time in flash pyrolysis reduced thermal cracking, which in turn decreased the formation of non-condensable gases [8]. The presence of high carbon and oxygen content in the biomass leads to more char formation [15]. Microwave-assisted hydrothermal carbonization improved biochar yield from rice husk, with low temperature and lower reaction time, compared to other process variants. Conversely, wet pyrolysis produced biochar with highest carbon content of 71.2% (Table 1).

Further, ultimate analysis of biochar depicted a slight reduction in H content with an increase in pyrolysis temperature due to the release of hydrocarbons such as CH_4 and C_2H_6 at a higher temperature. However, with an increase in temperature, a gradual increase in carbon content along with a considerable depletion in oxygen content was observed, due to the carboxylation of rice husk and subsequent generation of CO_2 , CO, moisture and carbohydrates (Table 1). Further, the decrease in moisture content (MC) and an increase in C/O ratio improved the high heating value of the terrified rice husk to be used as a source of fuel [10].

5 Modification of rice husk biochar

Although several inherent properties of biochar obtained from the pyrolysis variants suit to various environmental applications, unpyrolyzed biomass and mineral ash block the pores of biochar (Fig. 1). Hence, several modification methods are adopted to enhance the biochar properties based on its end-use, such as soil remediation and pollutant adsorption. Physical modification, chemical modification, and metal impregnation are the common methods adopted to obtain the modified/engineered biochar with improved surface area, morphological properties, and chemical properties compared to the rice husk biochar obtained from pyrolysis.

5.1 Physical modification

The physical or thermal modification method of the rice husk biochar tends to be less costly and more environmental friendly compared to chemical methods. In this method, biochar is subjected to partial gasification using steam and carbon dioxide as activating agents [34].

In steam activation, biochar is exposed to steam, which led to partial gasification of trapped volatiles as per Eq. 1. This step of partial gasification stimulates the formation of crystalline C and results in partial devolatilization of biochar. Hence with steam activation, the pores of the biochar can be increased by the removal of the unpyrolyzed biomass and trapped products formed during pyrolysis. Also, the process facilitates a greater abundance of aromatic and few oxygenated function group being developed on the surface [34, 35].

$$C + H_2 O \rightarrow CO + H_2 \tag{1}$$

On the other hand, gas purging is often carried out with gases such as carbon dioxide, which reacts with the available amorphous carbon in biochar in the limited oxygen atmosphere to form carbon monoxide (Eq. 2). Evolution of carbon monoxide enhances the surface area of biochar due to corrosion resulting in the improved microporous structure and increased pore volume (Fig. 2) [34, 35].

$$C + CO_2 \rightarrow 2CO$$
 (2)

Several researchers observed higher gasification rate by steam activation compared to CO_2 purging, which could be due to the difference in activation energy in reaction energies using the two activating agents [36–38].

5.2 Chemical modification

5.2.1 Alkali modification

Alkali modification of biochar involves a chemical reduction process with reducing agents such as NaOH, KOH and NH₄OH. Alkali modification improved porosity and specific surface area of biochar by the removal of unpyrolyzed organic matter and ash content from the pores (Fig. 3). Also, removal

Fig. 1 Schematic representation of biochar from pyrolysis process



of volatile carbon from pores improved the fixed carbon content in biochar. Further, the process caused a reduction in the oxygen-containing functional group, along with an increase in hydroxyl functional group (OH⁻) [16, 35], thus improving its adsorption capacity of pollutants, mainly, the non-polar pollutants [39].

5.2.2 Acid modification

In acid modification or chemical oxidation process, biochar surface is oxidized using HCl, HNO₃, H₂O₂ and H₃PO₄. The acid modification improved the hydrophilicity of biochar by increasing the oxygen-containing functional group such as carboxyl group (-COOH) on the surface. Biochar modified by HNO₃ comprised of higher oxygen-containing functional groups compared to other oxidants [35, 39]. The process also

Fig. 2 Microporous structure of biochar obtained after steam activation and CO₂ purging

removed unpyrolyzed organic matter and mineral ash, thus increasing the volume of pores as in the case of physical modification (Fig. 3). Conversely, oxygen-containing functional group caused hydration and subsequent blockage of the pores [39, 40]. Acid modification improved the structure of biochar and provided greater affinity towards adsorbing polar compounds by forming hydrogen bond with highly electronegative surface oxygen as a result of its hydrophilicity [41].

5.3 Metal impregnation

In recent years, several investigators have focused on metal impregnation of biochar, in which metal ions are incorporated on to the surface and pores of the biochar. Magnesium, silver, zinc, copper, iron etc. are the typical metal ions incorporated in biochar. Metal impregnated biochar showed significant





Fig. 3 Surface properties of biochar obtained from different chemical modification processes

improvement in adsorption capacity of various pollutants compared to un-modified biochar owing to the presence of two solid phases, viz. nano-crystals of metal oxides and biochar matrix [42]. Both of these phases contributed to the overall adsorption capacity of composites through various mechanisms such as hydrogen bonding, precipitation, electrostatic precipitation and ligand exchange (Fig. 4). Powdered biochar poses difficulty in separation from the aqueous matrix and unfavourable sorption towards anionic pollutants. The separation of powdered biochar from wastewaters requires a tedious process such as centrifugation/filtration and thereby hindering their usage in real treatment schemes [16]. Metal impregnation by magnetic metals like iron is employed to enhance the separability of powdered biochar after the treatment process through magnetic separation (Fig. 4). Magnetic biochar is synthesized through chemical co-precipitation of Fe²⁺/Fe³⁺ onto biomass followed by subsequent pyrolysis [43]. The hybrid nature of magnetic biochar also enables improved sorption of various inorganic and organic pollutants.

5.4 Effect of modification method on biochar properties

Table 2 shows the surface characteristics of modified rice husk biochar obtained from different modification processes. Physical modification by 15-min steam activation of rice husk biochar obtained from fast pyrolysis indicated ~ 3-fold increase in the surface area, with the respective values of 486 m²/g and 1365 m²/g for biochar and modified biochar. The micropore volume (MPV) increased from 0.05 cm³/g to 1.160 cm³/g during steam activation. In contrast, physical

modification of the same biochar by CO_2 purging for 45 min showed a peak surface area of 1564 m²/g with MPV of 1.045 cm³/g. The faster kinetics of steam activation compared to CO_2 activation resulted in a broader pore size distribution with the presence of significant micropores in steam activated biochar [34].

Conversely, acid modification by H₃PO₄ indicated significant improvement in surface area compared to that of H_2SO_4 modification (Table 2). However, the chemical modification of rice husk biochar by alkali activation showed considerable improvement in surface area compared to that of acid activation. The surface area and micropore volume of biochar obtained from fast pyrolysis were 34.4 m^2/g and 0.028 cm³/g, respectively. Acid and alkali activation showed \sim 1.4 times and \sim 3.4 times improvement in surface area of the biochar with the corresponding value of 46.8 m^2/g and 117.8 m^2/g respectively. The microporous volumes of acid-activated biochar and alkali-activated biochar were 0.033 cm^3/g and 0.073 cm^3/g , respectively (Table 2). Even though acid and alkali activation facilitated the removal of unpyrolyzed organic matter and ash content from the surface of biochar, oxygen-containing functional group in the acid activated biochar caused hydration and subsequent blockage of the pores thus hindering physical adsorption capacity [39, 40]. Overall, the chemical modification improved the surface area and porosity of the modified biochar resembling the removal of the unpyrolyzed organic matter and mineral ash and generating favourable surface functional groups such as aromatic (C=C), carboxyl and hydroxyl functional species as shown in Fig. 2.





On the other hand, a reduction in the surface area from 181 to 77.3 m^2/g and a reduction in microporous volume from 0.37 to 0.13 cm³/g were observed for the biochar modified with metal impregnation. The decrease in surface area and pore volume was due to the amendment of iron oxide into the pores of the biochar while generating appropriate surface functional groups like metal cations for the adsorption of anionic contaminants from wastewater [43].

6 Environmental application of rice husk biochar

Rice husk biochar is mainly used as functional materials in areas of agriculture and environmental remediation [7, 34, 43]. Use of biochar to soil acts as a carbon sink while reducing the CO₂ emission by biomass burning. Also, biochar addition improves the soil property and productivity by enhancing the structure and nutrient content of the soil [16]. Biochar

 $SA(m^2/g)/MPV(cm^3/g)$

Table 2 Characteristics of modified rice husk biochar

Type of	Process variants	Activation	SA(m ² /g)/MP	V(cm ³ /g)	References
modification		time (min)	Before modification	After modification	
Steam activation Gas purging (CO ₂)	Flash pyrolysis	800/15 800/45	486/0.05 486/0.05	1365/1.160 1514/1.045	[34]
Acid modification (1 M H ₃ PO ₄)	Pyrolysis (441 °C @ 20 °C/min)	200/180	12.47/0.005	102.4/0.034	[44]
Acid modification	Fast pyrolysis (450–500 °C)	70/60	34.4/0.028	46.8/0.033	[40]
(10%v/vH ₂ SO ₄) Alkali modification (1 M KOH)				117.8/0.073	
Alkali modification	Pyrolysis (450 °C @ 20 °C/min)	750/60	589/0.24	2183/0.58	[45]
(KOH) Iron oxide impregnation	Time, 3 h Pyrolysis (950 °C @ 20 °C/min)	/d	181/0.37	77.3/0.13	[43]
(post treatment)	Time-0.5 h				

*SA BET surface area, MPV microporous volume

application to soil showed an increase in water retention, soil fertility, cation exchange capacity, soil pH and improved soil microbial activity [46]. The rice husk biochar produced at a higher temperature of about 500-600 °C resulted in high availability of nutrients like phosphorus and potassium. The improvement in the nutrient availability of phosphorus and potassium ranged from 0.22 to 1.8 mg/g and 0.16 to 0.68 mg/g respectively as the temperature varied from 350 to 700 °C [47]. On the other hand, high surface area, microporous structure and surface functional groups led to the use of biochar as an adsorbent for various pollutants from aqueous or gaseous phase [48] [46]. The aromatic functional group in abundance along with hydroxyl group in biochar facilitated adsorption of metal cations by cation- π interaction [15, 21]. Table 3 summarizes various applications of rice husk biochar in environmental remediation. Adsorption of cations like

 Table 3
 Application of rice husk biochar for environmental remediation

Environmental application	Pyrolysis process variant	Temp (°C)/ modification	Inferences	References
Adsorption of pollutants from aqueous phase	Wet pyrolysis	220/	Adsorption capacity of 64.4 mg/kg, 9.7 mg/g and 220 mg/g for copper, methylene blue and iodine, respectively. Increased adsorption capacity of copper (72.5 mg/kg)	[7]
1 1	Pyrolysis	350/	Decrease in adsorption capacity compared to the biochar obtained from wet pyrolysis, with the respective values of 22 mg/kg, 3.3 mg/g and 134 mg/g for copper, methylene blue and iodine.	
		500/	Slight improvement in adsorption capacity with increase in pyrolysis temperature. Adsorption capacity of 30 mg/kg, 3.9 mg/g and 126.4 mg/g for copper, methylene blue and iodine, respectively.	
	Pyrolysis	550/metal impregnation	Modified biochar prevented ground water contamination by acting as excellent adsorbent for arsenate with an adsorption capacity of $1.15 \pm 0.1 \text{ mg/g}$	[43]
		950/metal impregnation	Increase in pyrolysis temperature from 550 to 950 °C improved the adsorption capacity of arsenic from 1.15 ± 0.1 mg/g to 1.46 ± 0.1 mg/g.	
	Fast Pyrolysis	450–500/acid modification (H ₂ SO ₄)	Tetracycline adsorption capacity was improved from 16.95 mg/g of raw biochar to 23.36 mg/g for the modified biochar. The mechanism of adsorption was chemisorption including H-bonding	[50]
	Fast pyrolysis	450-500/alkali modification (KOH)	The adsorption capacity of tetracycline increased from 16.95 mg/g for raw biochar to 58.82 mg/g for modified biochar. The mechanism of adsorption was due to the enhancement in the percentage carbon content of the modified biochar resulting it in having graphite like structure	[40]
Soil amendment	Microwave-assisted pyrolysis	600/	Adsorption capacity of 71 mg/kg and 497 mg/kg respectively for phos- phate nitrate. 1 kg of nutrient-loaded rice husk char released 68 mg of phosphate and 220 mg of nitrate, indicating soil nourishment potential of the used biochar.	[3]
	Fast pyrolysis	550/	4% biochar as soil amendment improved the quality of acidic soil. Total carbon and potassium content in soil increased by 72% and by 6–7-fold respectively, thereby resulting in carbon sequestration and nourishment of the soil for better yield	[9]
	Pyrolysis	500/	Application of 3% of rice husk biochar showed enhanced the soil properties. The CEC and pH of the loamy soil increased by 30% and 0.69, respectively. It was also confirmed that pH of the soil remained within the neutral range with no potential detrimental impact on the nutrient availability for the growth of crops. In addition, leaching of nitrate decreased from 9.37 mg/L to 5.21 mg/L.	[52]

copper and arsenic, anions like iodine and other organic pollutants like dyes and tetracycline indicated its significant removal from aqueous phase by biochar and modified biochar. The adsorption study for the removal of copper, methylene blue and iodine showed better adsorption potential of the biochar obtained from wet pyrolysis compared to that of pyrolysis (Table 3). The improved adsorption potential of wet pyrolysis biochar was due to the retention of higher oxygencontaining functional group compared to that of pyrolysis biochar [7]. Adsorptive removal of trace organic compound by biochar is gaining importance in recent years as a costeffective treatment method [49]. The alkali- and acid-modified rice husk biochar was used for the removal of tetracycline, a carcinogenic compound, from water. The result indicated higher affinity of alkali-activated rice husk biochar towards adsorbing tetracycline with a maximum capacity of 58 mg/g compared to the acid-modified biochar with a maximum capacity of 23.36 mg/g [40, 50] which was attributed to the large specific surface area and porous structure of the alkali activated biochar (Table 2). In addition, its graphite-like structure facilitated the formation of π - π interaction between the ring structure of tetracycline molecule and graphite sheets (Table 3). Similar results were also observed in adsorption of volatile organic compounds (VOCs) on acid- and alkalimodified coconut shell-based biochar [38]. Further, rice husk biochar obtained from microwave-assisted pyrolysis exhibited excellent nutrient retention capacities of 68 mg/kg of phosphate and 220 mg/kg of nitrate [3]. One kilogram of nutrientloaded rice husk char released 68 mg of phosphate and 220 mg of nitrate, indicating soil nourishment potential of the used biochar. These extractable nutrients were found to be comparable with the optimum soil nourishment required for the growth of crops [50]. Another study conducted to evaluate the effect of rice husk biochar on soil properties showed the cation exchange capacity (CEC) of the biochar (17.57 c/mol) was found to be higher as compared to that of the compost (10.3 c/mol) used in the study clearly depicting its potential of being a soil amender which resulted in increasing the CEC of the soil. Increased surface area, porosity, negative charges on the biochar surface and increase in pH due to biochar addition resulted in increased CEC of biochar amended soil [51, 52].

7 Conclusion

Rice husk biomass composed of various proportions of moisture content (MC), volatile matter content (VM), ash content (Ash) and fixed carbon content (FC) depending on its growth condition and geographic location. The MC, VM, Ash and FC in rice husk was reported in the range of 4.5-10.8%, 70.2-78.5%, 3.4-17% and 3.4-19.8% respectively. Various pyrolysis variants such as wet pyrolysis, pyrolysis, torrefaction, slow pyrolysis, fast pyrolysis, flash pyrolysis and microwave-assisted pyrolysis have been employed in the past for the conversion of rice husk to biochar. The process variants and operating conditions influenced the yield and property of rice husk biochar. Among physical modification method, steam activation resulted in more microporous biochar compared to CO₂ purging. The alkali and acid modification was performed respectively to improve hydrophobicity and hydrophilicity of rice husk biochar. Conversely, metal impregnation was done on rice husk biochar to improve adsorption potential or the post treatment separability. Rice husk biochar is successfully applied for adsorption of pollutants such as heavy copper, methylene blue, iodine, arsenate and tetracycline. The rice husk biochar increased the soil pH, microporosity and cation exchange capacity. Biochar amendment in soil also reduced the leaching of nutrients like nitrate and phosphate from soil.

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