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# Production of biochar from rice straw and its application for wastewater remediation -

# An overview

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# Abstract

The valorization of biochar as a green and low-cost adsorbent provides a sustainable alternative to commercial wastewater treatment technologies that are usually chemical intensive and expensive. This review presents an in-depth analysis focusing on the rice strawderived biochar (RSB) for removal of various types of contaminants in wastewater remediation. Pyrolysis is to date the most established technology to produce biochar. Subsequently, biochar is upgraded via physical, chemical or hybrid activation/modification techniques to enhance its adsorption capacity and robustness. Thus far, acid-modified RSB is able to remove metal ions and organic compounds, while magnetic biochar and electrochemical deposition have emerged as potential biochar modification techniques. Besides, temperature and pH are the two main parameters that affect the efficiency of contaminants removal by RSB. Lastly, the limitations of RSB in wastewater remediation are elucidated based on the current advancements of the field, and future research directions are proposed.

Keywords: Rice straw; biochar; wastewater remediation; activation; adsorption.

# 1. Introduction

The increase in world population has culminated the food demand substantially, including rice being the most important grain crop globally. As a result of intensive rice farming to cater the demand, massive amounts of rice straw (600 – 1000 MT) are generated annually as agricultural waste (Bhatnagar et al., 2022). This solid biomass waste can be transformed to cheap and environmental-friendly biochar that can be upgraded and engineered to be valorized in a plethora of applications, such as adsorbents (Singh et al., 2020b), fertilizers (Dinh et al., 2022), catalysts (Lee et al., 2020) and soil conditioners (Liu et al., 2022). With this, the dual advantage of circular bioeconomy and efficient handling/management of crop residues can be pursued.

Biochar can be derived from rice straw via a variety of thermochemical conversion routes, including pyrolysis (Zong et al., 2021), torrefaction or carbonization (Tan et al., 2021), hydrothermal liquefaction (Harisankar et al., 2021) and gasification (Pei et al., 2020). The properties of the biochar produced depends heavily on the process conditions, such as pressure, temperature, reactor configurations, as well as the catalysts used. Generally, pristine rice straws have high ash content (8.5 - 20.4%) as compared to other straw types such as wheat straw (5.0 - 8.5%), barley straw (7.4%), corn straw (5.1 - 7.9%) and sugarcane straw (4.1%)(Wang et al., 2020). Silica oxide is the main constituent of the ash in the presence of other oxides such as aluminium oxide and calcium oxide (Singh and Patel, 2022). Other elemental contents of rice straw include ~40% carbon, ~30% oxygen, ~5-6% hydrogen, ~1% nitrogen and <0.2% sulfur (Wang et al., 2020). The characteristics and properties of several straw-type biomass are compared and summarized in Table 1. Generally, these straw-type biomass contain comparable elemental composition (C, H, N, S, O) and are having low moisture content of <10%, rendering them a suitable pyrolysis feedstock for biochar production. In addition, the moderate fixed carbon content of rice straw (as compared to other

straw-type biomass such as sugarcane straw and wheat straw with <10% of fixed carbon) is also a favourable feature for carbon-based adsorbent synthesis (Nawaz and Kumar, 2021). *Table 1: Characteristics and properties of straw-based biomass.* 

Upon thermochemical treatments, rice straw can be converted to biochar with superior physico-chemical and structural characteristics, including increased carbon content, enhanced surface area, porosity and ion exchange capacity, which make rice straw-derived biochar (RSB) a promising bio-based precursor for adsorbents (Wang et al., 2020). In particular, RSB can be strategically applied for aquaculture wastewater treatment in the context of integrated rice-fish (agri-aquaculture) polyculture systems due to their convenient proximity (Li et al., 2021) and the high feasibility of RSB in removing some pollutant compounds (e.g., phosphorous, ammonia) commonly detected in aquaculture wastewater. Several studies have shown that RSB exhibited promising removal efficiencies towards pesticides (e.g., imidacloprid, atrazine) (Xiang et al., 2020) and pharmaceutical residues (e.g., estrone) (Monga et al., 2022) generated from aquaculture facilities (Kolodziej et al., 2004).

Several review articles on the application of biochar for wastewater treatment are available in the literature. Zeghioud et al. (2022) performed a comprehensive review of the characteristics of biochar derived from various feedstocks and the effects of operating parameters of water treatment that influence the efficiency of organic pollutants removal from wastewater. Similar review article but focusing on biochar derived from municipal solid wastes (MSW) was reported by Li et al. (2022a). Besides, the sustainability aspects (in terms of economic, social and environmental) of biochar for water and wastewater remediation were covered by Kamali et al. (2021). Deng et al. (2021) and Zhuang et al. (2022) also conducted interesting reviews on the performance of biochar for wastewater treatment from the perspectives of ecological benefits and removal mechanisms, respectively, but their

scopes were only limited to constructed wetlands and not other types of wastewaters. All these articles have generally spanned a broad range of feedstocks, but the in-depth review of biochar derived from a particular feedstock for wastewater treatment is still lacking and remains as the white space to be addressed and understood.

As such, the main objective of this review is to deep dive into the field of wastewater treatment specifically by RSB. Such thorough and distinct review is still scarce in the literature to the authors' best knowledge. Hence, this review is systematically structured to include various relevant and significant aspects, i.e., preparation of biochar (Section 2), modification or functionalization of biochar (Section 3), performance of pollutants removal from wastewater and the mechanisms involved (Section 4), application of biochar for treatment of various types of wastewaters (Section 5), and lastly the current associated limitations and prospects (Section 6).

### 2. Preparation of rice straw-derived biochar

Pyrolysis is defined as thermochemical conversion which involves lignocellulosic materials that experience thermal decomposition process with no or limited access of oxygen to produce pyrolysis products such as solid product with enriched carbon content known as biochar (Foong et al., 2022; Foong et al., 2020). Sakhiya et al. (2021a). Pyrolysis is divided into slow and fast pyrolysis. Slow pyrolysis involves heating rate from 0.02 - 1 °C/s and residence period from few hours to days (Dai et al., 2020b; Foong et al., 2021). Meanwhile, fast pyrolysis involves heating rate of more than 2 °C/s and residence period of less than 10 s (Dai et al., 2020b). The temperature range for slow and fast pyrolysis are 300 - 700 °C and 300 - 1000 °C, respectively (Foong et al., 2021; Ibn Ferjani et al., 2019). Sakhiya et al. (2022) prepared biochar from rice straw with slow pyrolysis in a batch-type pyrolysis reactor from 300 - 500 °C with a residence time of 60 mins and a heating rate of 10 °C/min. Firstly,

the air was removed from the reactor with the aid of vacuum pump and thereafter purged with nitrogen flow rate of 1.5 L/min to ensure the reactor was in an inert condition. After 1 min of running the batch-type pyrolysis reactor, the biochar produced would be cooled to ambient temperature. In another separate study, Cueva Z et al. (2022) conducted pre-treatment on the biochar produced from rice straw with ammonium sulphate (AS) and diammonium phosphate (DAP) at pyrolysis temperature, solution concentration, and dwell times ranging within 300-600 °C, 0.1-0.5 mol/L, 30-60 min, respectively. When compared with the pristine RSB, the pre-treated RSB demonstrated a much lower degradation temperature and mass-loss rates during the pyrolysis process. This was due to the accelerating processes in both dehydration and charring reactions. It was found that AS pre-treated RSB resulted in lower thermal stability. To achieve optimum condition, the pyrolysis temperature, dwelling temperature, and concentration of DAP were found to be 400 °C, 30 mins, and 0.2 mol/L, respectively. Park et al. (2017) produced RSB from slow pyrolysis in a muffle furnace with limited amount of nitrogen gas purged at 10 psi. The biomass chamber was heated to 600 °C with a period of 4 h and a heating rate of 10 °C/min. Thereafter, the RSB was cooled to room temperature and was grounded to a particle size less than 0.5 mm, then dry in an oven at temperature of 60 °C. In this study, the evaluation on the adsorption behavior of both Cu and Zn in both single and binary-metal systems was conducted at a temperature of 600 °C. It was found that there is a close relationship between the Cu and Zn adsorption and the exchangeable cation. Besides, it was concluded that the RSB that possess great cation exchange capacities would be ideal for the purification purpose for wastewater containing contaminated metal. However, future studies on the remediation capabilities towards binary and multi-metal wastewater are needed on an individual basis. And also, it was concluded that the RSB that possess great cation exchange capacities would be ideal for the purification purpose for wastewater containing contaminated metal are needed on an individual basis. This is further elaborated that the

metals in the RSB behaves differently due to the characteristics of the metals and adsorbent, and sorption sites. Dermawan et al. (2022) studied on the golden shower (*Cassia fistula*) seed waste and rice straw (*Oryza sativa*) in atmospheric-pressure microwave plasma for biochar production. Nitrogen gas was used as a purging gas to produce plasma with propagating microwaves at different flow rates of 7 - 9 L/min for a duration of 5 mins, and the power was supplied at 1.2 kW at a pressure of 30 psi. The experimental setup of the atmospheric-pressure microwave plasma reactor is illustrated in Figure 1. In their study, they found that the biochar produced from golden shower seed (11 L/min gas flow rate) and rice straw (7 L/min gas flow rate) activated by the microwave plasma reactor successfully reaches 344.8 mg/g, and 188.3 mg/g, respectively for maximum adsorption capacity. In addition, it was found that the biochars' surface area produced increased significantly after the pyrolysis process.

Figure 1: Exemplary atmospheric-pressure microwave plasma reactor used for biochar rice straw production by Dermawan et al. (2022).

Hydrothermal carbonization (HTC) is another thermochemical conversion which involves the use of water at elevated temperature and under hot compression for hydrochar production (Seow et al., 2022). This process involves reactions such as hydrolysis, dehydration, condensation, and aromatization. This process is considered another option to conventional slow-pyrolysis to produce a stable and carbon-rich biochar. The role of water in this process is to hydrolyze the glycosidic group on the biomass component, particularly the cellulose and hemicellulose to increase the porosity of the produced hydrochar. Although water could act as a good candidate for heat transfer, however, it would not be suitable for feedstocks that have a tendency to change the particle size significantly and short reaction time (Seow et al., 2022). This process can be divided into two main parts which consist of

high temperature hydrothermal carbonization ranging from 300-800 °C, and low temperature hydrothermal carbonization ranging from 200 – 250 °C (Tang et al., 2018). The advantages of using this process compared to pyrolysis process are that pre-drying treatment are not needed, production of hydrochar with high heating value, and reduction of alkali and metal content in the hydrochar products (Huff et al., 2014). In order to enhance the fixed carbon content and reduce the moisture and volatile matter contents in the hydrochar produced, it was suggested to conduct the hydrothermal carbonization at temperature of 300 - 400 °C and residence period of 1 - 3 hour (Tang et al., 2018). In a separate finding by Seow et al. (2022), lower operating temperature would reduce the conversion of chemical compounds and is more environmental-friendly. It was reported that hydrochar could act as an effective adsorbent for the application of soil modifications, resource retrieval, and environmental remediation merits (Kavindi et al., 2022). Kavindi et al. (2022) developed hydrochar from the hydrothermal co-carbonization of sewage sludge and rice straw for the bioremediation of Cr(VI) in soil. For the preparation of the hydochar in this study, the hydrothermal cocarbonization of samples at various mass ratios was performed at the ratio of biomass to deionized water of 1:10 weight/volume, temperature of 250 °C and duration of 1 h to achieve the desired characteristics of the produced hydrochar. In this study, the synergistic effect between the rice straw and digested sewage sludge and the Cr(VI) remediation by the soil alone were evaluated. It was found that the main mechanisms involved in the Cr(VI) remediation process are adsorption and reduction. The hazardous heavy metal in the soil was found to reduce significantly when co-carbonization of hydrochar of rice straw and digested sewage sludge in a ratio of 1:1 was used.

Thermal gasification for biomass feedstock is said to be a promising innovation to merge the bioenergy production and effective soil fertility management via the application of biochar for soil modification (Hansen et al., 2015). Hansen et al. (2015) produced straw and

wood biochar from two gasifier systems, i.e., low-temperature circulating fluidized bed gasifier (LT-CFB) and TwoStage gasifier. The LT-CFB consists of individual pyrolysis fluidized bed reactor and gasification fluidized bed reactor supported by a circulating heating medium to allow heat transfer starting from the gasification to pyrolysis process. The operating temperature for the LT-CFB system is within 700-750 °C to avoid the ash sintering to occur, and corrosion on the plant unit operation. Meanwhile, the TwoStage system operates at a high temperature (1000-1200°C) with each reactor functioning in pyrolysis and gasification processes separately to allow tar-cracking zone. This system has an advantage to produce minimal tar from the syngas produced which is suitable for gas engine and biofuel production. A promising result was found on the gasification biochar for soil amendment compared to the conventional pyrolysis biochar produced. A liming effect was observed in the gasification biochar which increased the pH level from 8 to 9 on the soil. Xiao et al. (2015) investigated on the biochar production from rice straw using a novel microwaveassisted gasification process. It was highlighted that the reaction involved in this process can be accomplished in a more efficient manner compared to other conventional heating methods by providing superior heat transfer profiles (Xiao et al., 2015). For the sample preparation, the rice straw feedstock was grounded into a particle size of 0.83 mm before undergoing drying process in an oven at a temperature and duration of 105 °C and 4 h, respectively before proceeding to the gasification process. Figure 2 illustrates the experimental setup on the novel microwave-assisted gasification process used by Xiao et al. (2015) for the production of rice straw biochar. It was found that catalytic effects from K<sub>2</sub>CO<sub>3</sub> and KOH in the RSB had positive influence on the carbon conversion, but the carbon dioxide  $(CO_2)$  in the syngas was also increased along. Table 2 summarizes the advantages and disadvantages of various thermochemical conversion such as pyrolysis, hydrothermal carbonization, and thermal gasification for biochar production.

*Figure 2: Experimental setup illustration on biochar production from microwave-assisted gasification setup conducted in the study by Xiao et al. (2015).* 

*Table 2: Advantages and disadvantages of various thermochemical conversions for biochar production.* 

# 3. Modification/functionalization of rice straw-derived biochar

Biochar production from rice straw is a promising approach of producing efficient adsorbent at low cost with enriched functional group and enhanced surface area (Khan et al., 2019; Melia et al., 2019). The major functional groups present in RSB are hydroxyl, carbonyl and phenolic hydroxyl groups, aliphatic double bonds, and benzene ring. These functional groups have provided the RSB with properties such as good adsorption capacity, oxidation resistance, hydrophobicity and environmental stability (Zhang et al., 2019). Previous research showed that RSB has good adsorption capability on heavy metals in wastewater, including cadmium, lead, chromium, copper, and zinc (Liu and Fan, 2018; Nham et al., 2019; Park et al., 2016). However, the application of pristine RSB in water treatment is limited due to the low porosity and surface functionality, small specific surface area, and limited adsorption capacity from water/aqueous solution with high concentration of contaminant/pollutant (Shaheen et al., 2022; Zhang et al., 2020). Therefore, surface modifications/activation of RSB is required to enhance its adsorption capacity and efficiency. RSB can be post-treated either by physical or chemical modification methods to improve the active sites for adsorption and the functional groups for specific adsorption functions. Table 1 summarizes the modification methods of RSB and its characteristics.

Table 3: Summary of the modification steps of rice straw derived biochar and its characteristics.

# 3.1 Physical modification of rice straw-derived biochar

Physical activation often involves the use of carbon dioxide (CO<sub>2</sub>) and steam as activation agent to improve the surface area of pristine biochar. Modification of pore structure via physical activation is achieved through the removal of volatiles and elimination of internal carbon mass (Sangon et al., 2018). Steam activation of RSB was found to improve the surface area of pristine RSB from 3.61 m<sup>2</sup>/g to 105.21 m<sup>2</sup>/g, and increase the total pore volume to 30 folds compared to pristine RSB (Sakhiya et al., 2021b). Moreover, steam activation altered the pore structure from mesoporous to microporous, which in turn provided more contact area on the biochar surface for adsorption. Physical activation was also reported to improve the oxygen-containing functional group on biochar surface, such as -COOH and -OH, thus increasing the adsorption efficiency of pollutants (Sakhiya et al., 2021b). However, the same author reported a higher adsorption efficiency of Zn ions by chemically activated RSB (Section 3.2), but the cost analysis revealed that physical activation method was relatively cheaper due to avoidance of chemicals usage for the activation processes (Sakhiya et al., 2021b).

# 3.2 Chemical modification of rice straw-derived biochar

Preparation of modified RSB with chemical activation was reported to show higher adsorption capacities compared to modified RSB with physical activation. A comparative study between physical activation (steam) and chemical activation (potassium acetate) of RSB was performed by Sakhiya et al. (2021b). Chemical activation of RSB produced biochar with higher total pore volume (0.183 cm<sup>3</sup>/g) and surface area (255.88 m<sup>2</sup>/g) as compared to that of activated physically (105.21 m<sup>2</sup>/g; 0.062 cm<sup>3</sup>/g). Besides that, the adsorption efficiency of Zn ions from aqueous solution was higher by RSB prepared via chemical activation (35.71 mg/g), as compared to RSB prepared via physical activation (27.78 mg/g).

The results showed that chemical activation produced more microporous structure and higher crystallinity index of 85.95% as compared to 82.2% for physical activation in RSB, thus providing more active sites for adsorption of Zn ions.

RSB is also rich in inorganic salts (Ca, Fe, Al, Mg and Mn salts), silicon and ash. These components can be removed by treating with acid and alkali to form soluble ions (Dai et al., 2020a). Simultaneously, the surface area, functional group and porosity would increase. Previous research reported that increase in the total surface area, functional group, porevolume and micropores structure can increase the adsorption capacity of pristine biochar (Cho et al., 2019; Ge et al., 2020). Chemical activation usually involves the use of chemicals such as NaOH, KOH, H<sub>3</sub>PO<sub>4</sub>, and K<sub>2</sub>CO<sub>3</sub>. Different chemical selected for the activation processes resulted in the formation of modified-RSB with different porous structure. For instance, RSB activation via potassium acetate favours formation of microporous structure, sulphuric acid favours formation of mesoporous structure, while KOH favours formation of the combination of both micropores and mesopores structure (Sakhiya et al., 2021b; Sangon et al., 2018).

Besides the abovementioned chemicals, nitric acid and amine/amino group can be used in chemical activation of RSB. For instance, Ahmed et al. (2021) modified RSB with nitric acid to remove uranium (VI) from nuclear wastewater. The modified RSB contained surface functional groups such as -COOH and -OH which facilitated the U(VI) removal of up to 242.7 mg/g as compared to that of pristine RSB (162.5 mg/g). Another modification of pristine RSB was performed by Zhang et al. (2019) using amine/amino group and an improvement in the adsorption capacity of cadmium cation of up to 72.1% was reported. The -NH<sub>2</sub> group on RSB surface facilitated the complexation reaction with Cd<sup>2+</sup>, thus improving the adsorption efficiency of Cd<sup>2+</sup>.

However, pristine RSB was usually predominant with net negative charge on the biochar surface, thus limiting the adsorption of anion from the aqueous solution. Therefore, Nham et al. (2019) modified the RSB with ferric chloride and iron (III) sulfate for the removal of arsenate [As(V)] anions from polluted groundwater. The results revealed that Fe-modified RSB had higher removal efficiency (26.9 mg/g) as compared to pristine RSB (11.2 mg/g). The Fe-modified RSB possessed positively-charged surface, which facilitated the ion exchange reaction between As(V) ions and OH<sup>-</sup> on the biochar surface, which in turn improved the adsorption of As(V) ions onto the biochar surface. Although chemical activation of RSB has proven to improve the adsorption capacities of pollutants from wastewater, most of the research focused on selected one or two types of pollutants. Thus, it has limited the potential use of RSB in treatment of discharged wastewater from different source such as industrial and agricultural wastewater. Therefore, in-depth research is suggested to be carried out in the future to determine suitable modification of RSB for various types of pollutant that co-exist in wastewater stream.

# 3.3 Hybrid modification of rice straw-derived biochar

Single modification on RSB has shown promising adsorption capacity, however, it was reported that combination of two or more modification methods could further improve the pollutant adsorption capacity. Generally, the modification involves the use of chemicals that can change the characteristic of the RSB to exhibit magnetic properties. For instance, Dai et al. (2020a) synthesized alkali-acid modified magnetic RSB and alkali magnetic RSB for the removal of tetracycline and reported the adsorption capacity of 98.3 mg/g and 98.0 mg/g, respectively, which was much higher compared to that shown by pristine RSB (37.8 mg/g). A similar alkaline magnetic RSB was prepared for the removal of rhodamine B (organic dye) and it reported high adsorption capacity of 53.7 mg/g (Ren et al., 2020). Chemicals and

magnetic modifications can improve the surface area and enhanced the formation of oxygencontaining functional groups on the surface of RSB, thus facilitating the adsorption of target contaminants via pore-filling effects and hydrogen bonding (Dai et al., 2020a; Ren et al., 2020).

Recently, more attention has been given to co-metal modified biochar as previous research showed that it has superior adsorption capacity compared to single metal modified biochar. For instance, Tan et al. (2018) prepared a Fe-Mn oxide-modified RSB (Fe-Mn BC) to compare the adsorption efficiency of co-modified RSB with single-modified RSB and pristine RSB. A high adsorption capacity of Fe-Mn BC (120.8 mg/g) was reported at 298 K, which was much higher than single-modified RSB with potassium (41.9 mg/g), manganese (81.1 mg/g) and pristine RSB (12.2 mg/g). The authors explained that the co-metal modification can increase the oxygen-containing groups on the RSB surface, resulting in a higher affinity towards Cd (II).

Previous studies reported on modifications of RSB showed promising adsorption performance in wastewater treatment. However, the preparation of modified-RSB often involves the use of chemicals, which is not sustainable. Therefore, electrochemical deposition method is introduced owing to its advantages such as simple operation, high removal efficiency, no secondary pollution and fast reaction speed for wastewater treatment (Wang et al., 2022). To be specific, limited chemicals are used in the electrode preparation, and it has higher energy efficiency for redox reaction. When current is applied to the electrode, ions of pollutants (mostly metals) migrate towards the electrode and form precipitates around the electrode/surface of electrode. Metal products (e.g., precipitates) can sometimes be recovered from the wastewater using this method (Yang et al., 2021). A research by Cheng et al. (2022) introduced a three-dimensional nano zero-valent iron-supported biochar (NZVI-BC) particle electrode for treatment of 2-naphthol wastewater. The electrode was prepared from

impregnation-pyrolysis method, where the RSB was dipped into ferrous sulfate heptahydrate, then dried in oven, followed by pyrolysis at 700 °C for 8 h. The electrode possessed high surface area (218.4  $m^2/g$ ) and high pH (10.5), which was effective in the adsorption of acidic 2-naphthol (93.8%).

Besides that, Wang et al. (2022) introduced a novel three-dimensional circular electrode from RSB for treatment of Cd (II) in wastewater. The preparation of electrode was carried out with two different methods, which were roller pressing (i.e., conventional method) and thermosetting method (i.e., novel method) (Figure 3). Electrode produced from thermosetting method was slightly better in Cd (II) removal and reported a high removal efficiency of 76.6%. Therefore, it was proposed as an alternative to conventional preparation method which is higher in cost, having complicated preparation procedure and is not suitable for large-scale applications. As a whole, post-treatment of RSB constitutes a new research area that targets to maximize the potential of the abundantly available rice straw waste as a cost-effective adsorbent. More effort is required to improve the surface chemistry and porous structure of RSB for its successful deployment in wastewater treatment. Besides that, analysis such as techno-economic analysis and life-cycle assessment are suggested for the application of RSB/modified RSB in wastewater treatment to study the feasibility of application in largescale wastewater treatment plants.

Figure 3: Preparation of RSB-electrode by a) roller pressing method and b) thermosetting method (Wang et al., 2022).

# 4. Pollutants removal from wastewater and the removal mechanism

The study of separation performance of biochar obtained from rice straw in removing wastewater pollutants over recent years is reviewed. Table 4 summarizes the major removal efficiency in treating different pollutants, which includes the optimal adsorption capacity and

its accompanying operating conditions, stability and regeneration potential, for different RSB prepared using varying synthesize methodologies.

Table 4: Efficiency of pollutants removal from wastewater and the removal mechanism using biochar-based adsorbent from rice straw.

Based on study from Table 4, it was seen that the recent studies were devoted to unravelling two major areas in order to enhance the removal efficiency of pollutants from wastewater, which are 1) to process the rice straw biochar via physical/chemical activation or modification and 2) to optimize the operating conditions, typically the pH and temperature, of adsorption process. With regards to the study focusing on physical/chemical activation, acids and bases, such as potassium hydroxide (KOH), phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), nitric acid (HNO<sub>3</sub>) and acetic acid (CH<sub>3</sub>COOH) (Ahmed et al., 2021; Dai et al., 2020a; Sakhiya et al., 2021b) had been reported to be able to improve the removal efficiency, which was postulated to form bigger pores and surface area due to attack that arose from corrosion. In addition, oxidation, nitrification and amination of biochar surfaces were able to enhance interaction with the water contaminants for effective adsorption. Additionally, the chemical modification with oxidants, which include hydrogen peroxide  $(H_2O_2)$ . potassium permanganate  $(KMnO_4)$  and (3-Aminopropyl) triethoxylane (APTES), were able to enhance the adsorption capacity via inclusion of oxygen and nitrogen functional groups that had higher affinity for the targeted pollutants (Li and Li, 2019; Tan et al., 2018; Tan et al., 2022). As compared to pristine RSB with adsorption capability of merely ~5-15 mg/g (Bashir et al., 2018; Khalil et al., 2018), activation with acids, bases and oxidants were found to consistently enhance the separation performance of pollutants from wastewater to at least > 40 mg/g, subjected to the nature of the contaminants, operating conditions and synthesis methodologies for the adsorbents. Remarkable adsorption capacity of tetracycline with 552 mg/g had been demonstrated in

work by Chen et al. (2018) using  $H_3PO_4$  modified RSB while Tan et al. (2018) reported 305.25 mg/g removal of Pb<sup>2+</sup> via KMnO<sub>4</sub> activation to prepare MnO<sub>x</sub>-coated rice straw based-adsorbents (Tan et al., 2018).

From the studied research work related to uncovering optimal adsorption operating conditions, it was observed that acidic conditions at a pH between 5 and 6.5 favored metal adsorption (Medha et al., 2021; Sakhiya et al., 2021b; Tan et al., 2022), while alkaline conditions with pH > 7 were more efficient for adsorption of organic compounds (Chen et al., 2018a; Dai et al., 2020a; Lap et al., 2021). Most of the pollutants' removal was carried out under normal room temperatures at 25-30 °C (Bashir et al., 2018; Gao et al., 2018; Zhang et al., 2018), which was replicative of wastewater remediation processes in tropical countries, although Khalil et al. (2018) and Mei et al. (2020) suggested that removal of NH4<sup>+</sup> and Cu ions by biochar was more effective in high ambient temperatures at 45 °C (Khalil et al., 2018; Mei et al., 2020). With respect to synthesis methodology, pyrolysis remains to be the most popular route to synthesize rice straw-based adsorbents of considerably good removal efficiency to date at temperature between 300 and 800 °C (Tan et al., 2018; Yi et al., 2021; Zhang et al., 2018). Higher pyrolysis temperature was suggested to enhance the effective surface area, micropore volume, pore size and mineral content of the resultant adsorbent by Medha et al. (2021) via decomposition of the oxygenated groups (H<sub>2</sub>O, CO<sub>2</sub> and CO), which enhanced adsorption capacity. Hydrothermal carbonization (HTC) has emerged recently as an alternative technique since it only requires moderate operating temperature of 150-200°C (Li and Li, 2019; Zhang et al., 2019), which is postulated to be able to lower the production costs while eliminating the use of any organic solvents, catalysts or surfactants, and produce outstanding removal efficiency for dyes removal using rice straw based adsorbent with capacity of > 174 to 295 mg/g. Its potential can be extended to study for removal of other

contaminants in order to increase the techno-economic feasibility of rice-straw based adsorbent in industrial scale applications.

It was also reported in Table 2 that the RSB is capable of removing contaminants including metal ions and organic compounds such as tetracycline and dyes from wastewater. The separation mechanisms for these compounds are slightly different as depicted in Figure 4. The separation mechanisms governing removal of metal ions include electrostatic interaction, ion exchange, complexation and co-precipitation while for organic compounds, they are driven to the rice straw-based adsorbent following electrostatic interaction, adsorption and diffusion process for pore filling,  $\pi$ - $\pi$  interaction and hydrogen bonding. The adsorption phenomena and behavior between RSB and pollutants had to be carefully studied and determined since the contaminants may be attracted to the adsorbent following different mechanism and routes based on its innate characteristics and properties. Nonetheless, it was generally found that the application of RSB in removal of ammonium gave low adsorption capacity of only 4.5 mg/g (Khalil et al., 2018) as compared to removal of other pollutants. Among all, acid-modified RSB was reported to be one of the most suitable adsorbents for removal of tetracycline with 552 mg/g. With regards to metal ions, Pb<sup>2+</sup> and U<sup>4+</sup> were most efficiently adsorbed with capacity of > 240 - 300 mg/g using oxidized and acid-modified RSB, respectively (Ahmed et al., 2021; Tan et al., 2018). It was also observed that RSB was more effective in removing dyes and heavy metals than livestock wastewater with adsorption capacity of only 9 and 16 for BOD and COD, respectively (Lap et al., 2021). Thus far, it was found that heavy metals were very popularly studied in recent literature, typically  $Cd^{2+}$  (Gao et al., 2018; Tan et al., 2022; Zhang et al., 2018), since it is a non-essential metal and poses a critical health risk. Nonetheless, the separation performance for adsorption of other heavy metals, such as mercury, nickel and arsenic, which are also considered as common heavy metals in wastewater with induction of human poisonings, was less elucidated to date. In

addition, the elucidation of other organic pollutants, microplastics, pharmaceuticals and personal care products (PPCPs) were also scarcely available.

Figure 4: Removal mechanism of pollutants using biochar from rice straw.

In addition, it was shown Table 4 that the application of RSB biochar for treatment and removal of contaminants from wastewater can be broadly categorized into industrial, agriculture wastewater and nuclear treatment. Increasing growth in human population and society advancement necessitate the development of these sectors and subsequently its wastewater production. Contaminants found in industrial wastewater are typically dyes, heavy metal and antibiotics, while agriculture wastewater are generated from production of food chain, livestock waste and pesticide. Nuclear wastewater on the other hand contains trace to high-level of radioactive elements, e.g., uranium, that are produced from mining and smelting or nuclear plant.

The rapid introduction and development of industry have resulted in large amount of wastewater discharged into the environment. These wastewaters often exist in complexation with heavy metals, organic chemicals, and some even consist of radioactive ions (Nguyen et al., 2021; Younis et al., 2020). For instance, heavy metal such as copper (Cu) was found in the wastewater produced from chemical and electroplating industries, while Cu causes adverse effect to human and environment, such as liver damage and insomnia, and inhibits soil enzymatic activities (Chai et al., 2021). Organic dye such as rhodamine (RhB), malachite green and crystal violet are present in the wastewater produced from dye manufacturing industry. These compounds possess properties such as teratogenic, carcinogenic and mutagenic, which are harmful to aquatic organism and humans (Chen et al., 2018b). Pristine RSB commonly exists as net negative charged adsorbent which is effective for the adsorption of positively charged organic pollutants and heavy metals. Mei et al. (2020) and Ren et al.

(2020) reported a high removal efficiency of Cu (99.6%) and RhB (92.0%) using RSB, respectively. Chemical modification on the pristine RSB produced modified biochar with more targeted surface functional groups and higher surface area, thus resulting in higher adsorption capacities. For instance, KOH modified RSB showed greater Cd adsorption capacity (41.9 mg/g) as compared to pristine RSB (12.2 mg/g).

The removal mechanism for heavy metals using RSB from industrial wastewater involve co-precipitation (Gao et al., 2018; He et al., 2021; Tan et al., 2022), complexation with functional groups (Mei et al., 2020; Tan et al., 2018; Zhang et al., 2019), electrostatic interaction (Mei et al., 2020; Zhang et al., 2018), and ion exchange (Gao et al., 2018; Tan et al., 2022). Removal mechanism of dyes originated from the textiles, paints, leather, pharmaceutical products, cosmetics, photographs, food and biological stains (Nikfar and Jaberidoost, 2014), and removal mechanism of antibiotics produced in the pharmaceutical industry from wastewater include hydrogen bonding (Chen et al., 2018a; Dai et al., 2020a; Yi et al., 2021),  $\pi$ - $\pi$  interaction (Chen et al., 2018a; Yi et al., 2021), diffusion for pore filling (Li and Li, 2019) and electrostatic interaction (Yi et al., 2021). The removal mechanism of organic contaminants, dyes and antibiotics, from wastewater using RSB are as illustrated in item 5-8 in Figure 4. Thus far, most of the experiments for RSB applications in industrial wastewater was conducted in laboratory scale with simulated wastewater and controlled conditions, instead of using the real-world polluted water. Actual performance of RSB on real industrial wastewater needs to be tested and verified.

Agricultural industry develops rapidly due to the increase in human population and demand for food. At the same time, pollution caused by the agricultural industry is becoming increasingly severe from the increasing use of pesticides, fertilizers, discharge of livestock wastewater into the farmland (Xiang et al., 2020). Therefore, RSB is introduced as alternative to treat the agriculture wastewater. For instance, Lap et al. (2021) prepared RSB via pyrolysis

and subjected the RSB to treat livestock wastewater from a pig farm in Ho Chi Minh City, Vietnam. Removal efficiencies of chemical oxygen demand (COD) and biological oxygen demand (BOD<sub>5</sub>) were achieved by RSB in both batch (40%) and continuous system (80%). The large pore volume and surface area of RSB not only provided adsorption sites for the organic pollutants, but it also allowed the development of more biofilms for microorganism, thus increasing the digestion of organic matter. In addition, their cost analysis revealed that applying RSB in livestock wastewater treatment can help to increase farmers' profit of up to 676 million USD/year (based on 0.01 USD/kg of rice straw stick). The used biochar with high concentration of organic matter was also proposed to be used as fertilizer for agriculture crops by the authors. The removal mechanism involved for treatment of agricultural wastewater using RSB includes adsorption (Medha et al., 2021), electrostatic interaction (Medha et al., 2021), ion exchange (Khalil et al., 2018),  $\pi$ - $\pi$  interaction (Huang et al., 2019), hydrogen bonding (Ambaye et al., 2021), which mostly revolves around removal of organic contaminants.

Nuclear waste is known to pose long term carcinogenic and toxic effects to living organisms, including human. It is generated during the operations involving the application of radioisotopes in the field of education, medicine, and research (Abdel-Karim et al., 2016). Thus, safe disposal or treatment of nuclear waste is becoming a global environmental challenge. Uranium (VI) is one of the radionuclides that can be found in sewage sludge. Chemical modification of RSB with HNO<sub>3</sub> has been introduced as an effective and low-cost adsorbent for U(VI) removal with high removal efficiency of 242.7 mg/g. The ionic strength of the inner-sphere and outer-sphere, pH and temperature changes have crucial influence in the adsorption process (Ahmed et al., 2021). Removal mechanism of uranium from wastewater using RSB includes surface complexation (Ahmed et al., 2021). Another research showed that chemically activated nanoscale RSB with NaOH can be used to adsorb

radioactive metallic ions such as barium and strontium that are present in effluent from petroleum/desalination industries (Prelot et al., 2018). High adsorption capacities of Ba (II) (73.9 mg/g) and Sr (II) (682.7 mg/g) ions were achieved, with low nanoscale fabrication cost (380-560 USD/tons), indicating the potential application of rice straw via the reported approach (Younis et al., 2020).

Other than the adsorption potential of the rice straw-based adsorbents, stability and regeneration capacity are another vital criterion to be evaluated in order to ensure economic feasibility and sustainability in industrial scale applications. However, only a fraction of studies had included the interrogation for stability while the regeneration potential had received less scrutiny. The stability of RSB had been investigated (Li and Li, 2019; Medha et al., 2021; Yi et al., 2021) and found to be having excellent adsorption capacities maintained for up to 225 hours by Chen et al. (2018a). With respect to the regeneration study, the good reusability of rice straw-based adsorbent had been demonstrated with removal capacity of  $\sim$ 85% to 99% after several adsorption-desorption cycles (Ahmed et al., 2021; Gao et al., 2018; Tan et al., 2018). In addition, from the review, it was highlighted that magnetic components, such as iron oxides, was also another emerging research area, potentially due to its interesting characteristics which enable separation from their surrounding medium by inducing a magnetic field. The magnetic RSB had been tested with various contaminants, which include tetracycline, dyes and metal ions, and demonstrated great potential of close to 100 mg/g removal capacities (Dai et al., 2020a; Tan et al., 2022; Yi et al., 2021). Nonetheless, the reusability capabilities of these biochar were less successful with only 45% to 72% retention in the adsorption capacities. This observation prompts more study in this avenue to further explore the sustainability of magnetic-RSB in removing various water contaminants.

# 5. Regeneration of used rice straw-derived biochar adsorbent

Regeneration of adsorbent (effective separation and recycle) remains as a challenge in the development of biochar-based adsorbent. Furthermore, utilization of biochar in large scale wastewater treatment plants is hard to be achieved due to biochars' variability and small particle size, causing slow flowrates and pressure drops in the columns. Filtration step is commonly used but the process is slow and increases the operation cost for changing of membranes or filters (Bombuwala Dewage et al., 2019; Nguyen et al., 2022). Introducing magnetic modification on raw biochar could enhance the removal efficiency of pollutants and attenuates the regeneration issues as it allows the biochar with small particle size to be recovered from batch processes (Bombuwala Dewage et al., 2019). For instance, Dai et al. (2020a) performed regeneration test on magnetic engineered biochar and reported high tetracycline removal (69%) after 5 cycles. The alkaline magnetic modified biochar prepared by Ren et al. (2020) showed similar adsorption capacities after 3 cycles in pure water (92.7-98.3%), but the capacity decreased in simulated water (71.6%), which was caused by the complexity of the matrix with co-existence of anions, cations and other organic pollutants. Magnetic engineered biochar can also be separated by magnet, which eases in the separation of adsorbent from the wastewater treatment plant.

Electrochemical deposition method has been introduced as a simple and clean method for wastewater treatment. This method utilizes small amount of chemicals and high energy electron as reductant, which facilitate the removal of pollutants from the electrode, thus increasing the recyclability of electrode. Wang et al. (2022) prepared a three-dimensional circular electrode made from RSB for removal of Cd (II) from wastewater and reported high removal efficiency (76.6%). The researcher performed pickling (3 M sulfuric acid) to the electrode after it was used in order to remove the Cd (II) deposited on the electrode. The electrode was reused for adsorption test and was able to sustain a similar removal efficiency (74.2%), suggesting that the electrode can be reused for wastewater treatment. Although

these methods show high potential for regeneration of used RSB, the application in larger scale is restricted owing to the lack of understanding on optimizing parameters for regeneration method, and the disposal issue of used RSB after many cycles. Improper disposal of used biochar may create secondary pollution to the environment by the heavy metals and organic pollutants that desorb or leach from the RSB surface. Therefore, regeneration of adsorbent is an important aspect in developing adsorbent for wastewater treatment.

# 6. Limitation & future perspective

Biochar produced from rice straw is deemed as a renewable resource for application in wastewater remediation. Nonetheless, more research is required in the mechanism of contaminants removal throughout wastewater treatment since the mechanism might be affected by the presence of toxic compounds in the biochar derived from biomass, such as polycyclic aromatic hydrocarbons, chlorinated hydro- carbons and dioxitins. In addition, extended research is needed in the discovery of new activation approaches for diversifying the application of biochar in terms of distinct contaminants removal along with its adsorption and desorption mechanisms. In this sense, Ahmed et al. (2021) reported that more studies are desired in exploring the numerous variables which affect the radionuclides sorption on biochar, especially the biochar modified through oxidation approaches for the removal of U(VI) from wastewater.

The nonradical degradation of organic contaminants via particular active sites such as graphitic N in biochar for the electrons flow (Sun et al., 2019) are also scarcely investigated compared to other carbonaceous allotropes due to minimal experimentation on the biochar's mechanism as an  $O_3$  activator (Gasim et al., 2022). Gasim et al. (2022) has further stated the limitations of biochar in environmental remediation such as (a) low efficiency in application

of primal biochar for removal of organic pollutants, (b) low permanence of biochar active sites throughout advanced oxidation processes (AOPs), (c) interactions between oxidant and pollutant in biochar are easily affected by the alteration of water pH which further impedes its application in wastewater treatment and (d) unable to mineralize or degrade organic contaminants through adsorption, whereby the aforementioned constraints can be overcome based on respective recommendations: (a) more research with regular explorations on the associations between the multi-dopants in the biochar structure and how it affects the performance of biochar, (b) production of biochar with high aromaticity and graphitization degree, (c) fabricate groups which are against pH alteration or distinct customization of biochar active sites and (d) adsorption with supplementary AOPs approaches along with the optimization of adsorption.

Economic accessibility and viability which affect the application of new approaches for biochar production should also be explored, with implementation of ordinary characterization procedures to enhance the understanding in biochar properties. In this context, biochar's surface properties should be further optimized since it is critical in reducing the environmental pollution through wastewater remediation (Singh et al., 2020a) and life-cycle analysis of biochar needs to be performed in order to assess the environmental impacts and economic advantages (Yaashikaa et al., 2020). According to Lap et al. (2021), more research should be conducted in evaluating the capability control of nutrient such as phosphorus and nitrogen, and the renewal of biochar in the filter column for developing a RSB with more extensive economic performance. In-situ experiments need to be implemented to examine the actual environmental impact of biochar, efficiency of biochar as well as the recovery and safety of biochar after being recycled (Amen et al., 2020). Experiments should be collective such that the biochar can remediate heavy metals in various water bodies from industries for further development of biochar application (Berslin et al.,

2022). Appropriate engineering works and design should also be managed by following the quality standards to ensure the qualification of biochar as a promising bio-remediating medium in the industrial context.

### 7. Conclusion

The use of RSB in wastewater remediation has shown promising feasibility in labscale experimentations. Various modification/activation techniques, including physical, chemical or hybrid, have significantly improved the RSB adsorption capacities through enhancement in the physicochemical and structural characteristics, as well as incorporation of targeted functional groups to tune the surface chemistry of the biochar. Generally, RSB demonstrates high adsorption capacities towards metal ions (Pb<sup>2+</sup>, U<sup>4+</sup> and Cd<sup>2+</sup>) and organic pollutants. The fundamental understanding of RSB adsorption and oxidation mechanisms can further be explored on other wastewater contaminants, such as mercury, microplastics, etc., while not neglecting the biochar's recyclability and stability aspects.

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Figure 1: Exemplary atmospheric-pressure microwave plasma reactor used for biochar rice straw production by Dermawan et al. (2022).



Figure 2: Experimental setup illustration on biochar production from microwave-assisted gasification setup conducted in the study by Xiao et al. (2015).





Figure 3: Preparation of RSB-electrode by a) roller pressing method and b) thermosetting method (Wang et al., 2022).



Figure 4: Removal mechanism of pollutants using biochar from rice straw.

Table 1: Characteristics and properties of straw-based biomass
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Biomass Ultimate analysis (%) Proxim				Proximate	analysis (%	()	Struct	ion (%)	Reference				
	С	Н	N	S	0	Moisture	Volatile matter	Fixed carbon	Ash	Hemicellulose	Cellulose	Lignin	
Rice straw	36.2	5.2	0.7	-	40.3	-	-	-	17.6	21.6	31.4	19.1	(Harisankar et al., 2022)
	47.46	6.44	0.83	-	45.15	4.98	81.54	16.46	10.82	-	-	-	(Liu et al., 2021)
Wheat straw	45.5	5.7	1.0	-	47.9	7.1	76.7	9.2	7.0		-	-	(Cheng et al., 2019)
Barley straw	45.41	6.10	1.18	-	46.21	4.90	78.80	11.83	6.43	-	-	-	(Ahmed and Hameed, 2018)
Corn straw	45.75	5.93	0.94	0.11	43.69	4.21	-	-	5.91	24.86	39.54	19.30	(Chen et al., 2019)
Sugarcane straw	41.88	5.87	0.47	-	41.72	3.12	87.61	3.22	9.17	12.05	52.60	22.50	(Ferreira et al., 2020)
Rape straw	42.21	5.54	0.42	0.07	51.76	-		-	3.69	28.89	45.27	22.15	(Li et al., 2022b)
Mustard straw	54.46	6.29	0.5	-	38.75	3.99	75.55	15.44	5.02	23.12	44.5	21.24	(Nawaz and Kumar, 2021)
								42					
								TL.					

Thermochemical conversion	Advantages	Disadvantages	Ref.
Pyrolysis	<ul> <li>Short residence time (less than 20 s) required for fast pyrolysis.</li> <li>Able to produce other products such as hydrocarbon liquid or diesel via hydrogenation pyrolysis.</li> <li>Uniform chemical properties of biochar produced via microwave assisted pyrolysis process.</li> </ul>	<ul> <li>Long residence time (ranging from few hours to few days) for slow pyrolysis.</li> <li>High heating value decreased the biochar production yield due to the depolymerization reaction taking place in the biomass that occurred during the fast pyrolysis process.</li> </ul>	(Seow et al., 2022; Xie et al., 2022)
Hydrothermal carbonization	<ul> <li>Water is a suitable medium for heat transfer.</li> <li>Possess high density biochar.</li> <li>Less energy requirement.</li> <li>High moisture content feedstock can be used.</li> </ul>	• Mass transfer limitation if feedstock particle size varies significantly and short reaction time takes place during this process.	(Krysanova et al., 2019; Nizamuddin et al., 2017; Seow et al., 2022)
Thermal gasification	<ul> <li>Low tar produced in gasification of biochar due to the volatile removal in pyrolysis process.</li> <li>Clean alternative to produce H<sub>2</sub> enriched syngas via steam gasification.</li> <li>Biochar has enough carbon content and heating value to be recycled back into the gasification system as fuel.</li> </ul>	<ul> <li>High reaction temperature could destroy the carbon-atoms via the gasification of C-H<sub>2</sub>O or C-CO<sub>2</sub>.</li> <li>Lower biochar yield produced compared to slow pyrolysis due to the presence of gasification agent and conversion of fixed carbon to CO gas during the partial oxidation reaction.</li> </ul>	(Anniwaer et al., 2021; Cao et al., 2017; Xie et al., 2022; Zaini et al., 2020)
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 Table 2: Advantages and disadvantages of various thermochemical conversions for biochar production.

Table 3: Summary of the modification steps of rice straw derived biochar and its characteristics.

Types of RSB	RSB	RSB modification steps	Porous prop	perties before	modification	Porous proj	perties after m	odification	Surface	Ref.
	preparation		BET Surface area (m <sup>2</sup> /g)	Average particle size (nm)	Total pore volume (cm <sup>3</sup> /g)	BET Surface area (m <sup>2</sup> /g)	Average particle size (nm)	Total pore volume (cm <sup>3</sup> /g)	group	
Steam activated biochar	Fast pyrolysis at 700 °C.	Rice straw was pyrolyzed, when temperature reaches 700 °C, steam was injected at flowrate of 0.5 kg/h for 1 h.	3.61	1.04	0.0059	105.21	1.33	0.062	Si-O-Si. Si-O-C, - OH, C-H, aromatic C=C, COO, C=O	(Sakhiya et al., 2021b)
CH <sub>3</sub> COOK activated biochar	Fast pyrolysis at 700 °C.	Rice straw was pyrolyzed with CH <sub>3</sub> COOK at 700 °C, then neutralized with HCl, followed by drying in oven at 105 °C.	3.61	1.04	0.0059	255.88	1.04	0.183	Si-O-Si. Si-O-C, - OH, aromatic C=C, C=O, COO, C- H	(Sakhiya et al., 2021b)
HNO <sub>3</sub> modified biochar	Purchased from biochar production company (pyrolyzed at 300 °C)	Biochar was washed with ultrapure water until neutral, then freeze dry. Next, pre-treated biochar was treated with 25% (v/v) HNO <sub>3</sub> at 90 °C for 4 h and the excess acid was removed with centrifugation.		-	-	-	-	-	C-O, C=O, O- H, O- C=O, C- O-C	(Ahmed et al., 2021)
Fe-modified biochar	Fast pyrolysis at 450 °C, retention time 1 h.	Biochar was treated with FeSO <sub>4</sub> .7H <sub>2</sub> O and FeCl <sub>3</sub> .6H <sub>2</sub> O, follow by pH adjustment with NaOH to 10-11. The treated biochar was then wash and dried at 60 °C in oven.	-	-	-	-	-	-	C=O, C- O, O-H, Fe-O	(Nham et al., 2019)
Amino- modified biochar	Fast pyrolysis at 600 °C,	Biochar was treated with $HNO_3$ (nitration) and $H_2SO_4$ (nitro- reduction) for 2 h at room temperature.	154.25	2.567	0.146	170.34	2.512	0.163	O-H, N- H, C-H, C-N	(Zhang et al., 2019)

	retention time 1 h.									
Alkali modified magnetic biochar	Slow pyrolysis at 300 °C, retention time 1 h.	Impregnation method with 2 M sodium hydroxide, followed by co- precipitation of ferric salts and ferrous on rice straw biochar.	28.132	213.29	0.03125	165.42	36.27	0.3106	C=O, C=C, O- H, Fe-O	(Dai et al., 2020a)
Alkali-acid modified magnetic biochar	Slow pyrolysis at 300 °C, retention time 1 h.	Alkali-modification: Impregnation method with 2 M sodium hydroxide and glacial acetic acid. Magnetic modification: Co- precipitation of ferric salts and ferrous on rice straw biochar.	28.132	213.29	0.03125	140.08	42.83	0.3102	C=O, C=C, O- H, Fe-O	(Dai et al., 2020a)
Alkaline modified biochar	Fast pyrolysis at 650 °C, retention time 1 h.	Rice straw was treated with NaOH for 1 h, followed by heated with FeCl <sub>3</sub> at 50 °C for 30 min. Then, the sample was washed and subjected into pyrolysis.	198.5	2	-	396.9	466.87	-	-	(Ren et al., 2020)
Fe-Mn modified biochar	Slow pyrolysis at 300 °C, retention time 4 h	Impregnation method with 0.15 M ferric nitrate and 0.25 M potassium permanganate, stirring for 2 h in room temperature and 22 h in 95 °C water bath, then heated at 300 °C for 0.5 h.	0.73	18.85	0.0015	8.28	25.83	0.0179	-OH, C=C, Si- O-Si, - COOH, Fe-OH, Mn-OH	(Tan et al., 2022)
Fe- supported biochar (NZVIs-BC) particle electrode	Slow pyrolysis at 700 °C, retention time 8 h	Electrode prepared from impregnation-pyrolysis method. RSB dipped into ferric sulfate heptahydrate for 24 h, dried in oven, then pyrolyzed at 700 °C for 8 h.		-	-	218.4	3.69	0.201	C-C, C- H, C=O, C=C, O- H	(Cheng et al., 2022)
Straw biochar electrode	Fast pyrolysis at 900 °C, retention time 20 min	Electrode is prepared with roller pressing method and thermosetting method (Figure 3).	-	-	-	-	-	-	-	(Wang et al., 2022)
"-" refers to N/A	Α.	5								

Adsorbent	Synthesis	Pollutants	Removal mechanism	Optimal operational condition	Adsorption capacity (Q <sub>m</sub> / mg/g)	Stability	Regenera- tion	Application	Ref.
- Pristine rice straw biochar - KOH modified rice straw biochar	- Pyrolysis at 500°C - Chemical activation in KOH solution	Cadmium, Cd <sup>2+</sup>	<ul> <li>Surface</li> <li>precipitation forming</li> <li>insoluble Cd</li> <li>Ion exchange with</li> <li>cations in biochar</li> <li>(e.g., calcium)</li> </ul>	pH: 6.5 Temperature : 25°C	- KOH- modified biochar: 41.9 - Pristine biochar: 12.7	NA	NA	Heavy metal removal from aqueous solution	(Bashir et al., 2018)
H <sub>3</sub> PO <sub>4</sub> modified rice straw biochar	<ul> <li>Pyrolysis at 700°C</li> <li>Chemical activation in H<sub>3</sub>PO<sub>4</sub> solution</li> </ul>	Tetracyclin e, TC	Chemisorptions including H bonding and $\pi$ - $\pi$ EDA interaction	pH: 9 Temperature : 25°C	552.0	Good stability with increasing and stable adsorption capacities tested for 225 hours	NA	Antibiotics removal	(Chen et al., 2018a)
Rice straw biochar	Slow pyrolysis at 500- 600°C	Ammoniu m, NH4 <sup>+</sup>	Ion exchange mechanism of NH <sub>4</sub> <sup>+</sup> and COO <sup>-</sup>	pH: 7.5 Temperature : 45±5°C	4.5	Good stability with stable adsorption capacities tested for 120 min	NA	Ammonium removal from fish farms	(Khalil et al., 2018)
MnO <sub>x</sub> - coated rice straw biochar	- Pyrolysis at 420°C - Chemical reaction with KMnO <sub>4</sub>	Lead (II), Pb <sup>2+</sup>	OH and COOH binding with Pb <sup>2+</sup>	pH: 5 Temperature : 20°C	305.25	NA	Good regenerabilit y. Desorption solution: HCl Efficiency: from 99.14% to 94.55% after	Lead removal from aqueous solution	(Tan et al., 2018)

Table 4: Efficiency of pollutants removal from wastewater and the removal mechanism using biochar-based adsorbent from rice straw.

							4 times reuse		
HNO <sub>3</sub> and H <sub>2</sub> O <sub>2</sub> modified rice straw biochar	- Pyrolysis at 800°C - Chemical activation in HNO <sub>3</sub> and H <sub>2</sub> O <sub>2</sub> solution	Cadmium, Cd <sup>2+</sup>	Electrostatic attraction between Cd <sup>2+</sup> ions and negatively charged surface	pH: 6 Temperature : 25°C	93.2	Good stability with stable adsorption capacities tested for 1600 mins	NA	Heavy metal removal from aqueous solution	(Zhang et al., 2018)
Rice straw biochar	Pyrolysis at 300, 500 and 700°C	Cadmium, Cd <sup>2+</sup>	Precipitation with minerals, complexation with oxygen-containing functional groups, coordination with $\pi$ electrons and cation exchange	pH: 6 Temperature : 28°C	139.91	Good stability with regression coefficient (R2) above 0.95	Acid treatment regeneration. Desorption efficiency: 85.7-96.7%	Heavy metal removal from aqueous solution	(Gao et al., 2018)
KMnO <sub>4</sub> modified rice straw biochar	Hydrothermal carbonization at 180°C and treatment with KMnO <sub>4</sub>	Malachite Green, MG	Diffusion of MG to the surface, adsorption on surface until saturated, then saturation of MG adsorption	pH: 5.5 Room temperature	295	Good stability with stable adsorption capacities tested for 120 mins	NA	Dyes removal from aqueous solution	(Li and Li, 2019)
Rice straw hydrochars	Microwave assisted hydrothermal carbonization at 160 to 200°C	Congo red, berberine hydrochlor ine, 2- naphthol, Zinc (II), Zn <sup>2+</sup> , and Copper (II), Cu <sup>2+</sup>	Irreversible adsorption process with berberine hydrochloride, 2- naphthol and Cu <sup>2+</sup> . Enthalpically driven adsorption process with Congo red and Zn <sup>2+</sup>	Temperature : 25°C	222.1, 174.0, 48.7, 112.8 and 144.9, respectively	NA	NA	Removal of organics and heavy metals from aqueous solution.	(Li and Li, 2019)

Amino modified rice straw biochar	- Pyrolysis at 600°C - Chemical nitrification and amination in HNO <sub>3</sub> and H <sub>2</sub> SO <sub>4</sub> solution	Cadmium, Cd <sup>2+</sup>	NH <sub>2</sub> groups complexation with Cd <sup>2+</sup>	pH: 7 Temperature : 40°C	84.266	Good stability with stable adsorption capacities tested for 24 hours	NA	Heavy metal removal from water	(Zhang et al., 2019)
Alkali-acid modified magnetic rice straw biochar	<ul> <li>Pyrolysis at 300°C</li> <li>Chemical activation in KOH and CH<sub>3</sub>COOH/H<sub>3</sub>PO<sub>4</sub>/HN O<sub>3</sub></li> <li>Co-precipitation of ferrous and ferric salts</li> </ul>	Tetracyclin e, TC	Hydrogen bonding and pore filling effect	рН: 7	98.334	Good stability with stable adsorption capacities tested for 120 mins	Reusability test indicates TC removal rate is as high as 69% after 5 cycles.	Removal of antibiotics from water	(Dai et al., 2020a)
Rice straw biochar	Pyrolysis at 500°C	Copper (II), Cu <sup>2+</sup>	Precipitation, electrostatic interaction, cation- $\pi$ interaction, and complexation	pH: 6 Temperature : 45°C	52.5	Good stability with stable adsorption capacities tested for 1600 mins	NA	Removal of copper from water.	(Mei et al., 2020)
Rice straw biochar	Pre-activation of RSB with NaOH (as an activator) Pyrolysis at 500°C	Ba(II)/Sr(II )	Weak ion-exchange or pore-filling mechanism	- pH: 9 - Temperature : 50°C - Duration: 24hr	1267.9 μmol/g	NA	NA	Oil-field saline water reclamation	(Younis et al., 2020)
Oxidized rice straw biochar	<ul> <li>Pyrolysis at 500°C</li> <li>Chemical activation in HNO<sub>3</sub> solution</li> </ul>	Uranium (IV), U <sup>4+</sup>	Surface complexation between Uranium (IV) and COOH and OH functional groups	рН: 5.5	242.65	Good stability with stable adsorption capacities tested for 300 mins	Adsorption performance decreased from 96% to 91% after 5 regeneration cycles.	Removal of nuclear waste from aqueous solution.	(Ahmed et al., 2021)
Oxidant and acid modified	<ul> <li>Pyrolysis at 300°C</li> <li>Chemical activation in H<sub>2</sub>O<sub>2</sub> and HNO<sub>3</sub>/H<sub>2</sub>NO<sub>4</sub></li> </ul>	Cadmium, Cd <sup>2+</sup>	Non-electrostatic mechanism (specific adsorption and surface precipitation)	pH: 5.5 Temperature : 25°C	46.31	NA	NA	Heavy metal removal	(Sakhiy a et al., 2021b)

rice straw biochar						ç	6		
Rice straw biochar	Pyrolysis at 300°C	Livestock wastewater treatment (COD and BOD <sub>5</sub> )	Not discussed.	pH: 7.6 Temperature : 29°C	- Q <sub>BOD</sub> : 9 - Q <sub>COD</sub> : 16	NA	NA	Livestock wastewater treatment	(Lap et al., 2021)
(3- Aminopropy l) triethoxylan e and iron rice straw biochars composites	<ul> <li>Pyrolysis at 400°C and 600°C</li> <li>Chemical silanization with APTES and modification with Fe</li> </ul>	Chromium (VI), Cr <sup>6+</sup> and Zinc (II), Zn <sup>2+</sup>	Electrostatic attraction, adsorptive reduction, ion exchange, and complexation with functional groups	pH: 7.5	100.59 and 83.92, respectively	Good stability with stable adsorption capacities tested for 1600 mins	NA	Contaminant s removal from soil	(Medha et al., 2021)
Magnetic rice straw biochar	Impregnation-pyrolysis of stainless-steel pickling waste liquor and rice straw	Crystal violet	Iron oxides, $\pi$ - $\pi$ interaction, hydrogen bonding and electrostatic interaction	pH: 6.0 Temperature : 30°C	111.48	Good stability with stable adsorption capacities tested for 250 mins	Adsorption performance decreased from 96.75% to 71.91% after 3 regeneration cycles.	Dye removal from aqueous solution	(Yi et al., 2021)
Iron and manganese oxides modified rice straw biochar	<ul> <li>Pyrolysis at 300°C</li> <li>Chemical modification of biochar in Fe(NO<sub>3</sub>)<sub>3</sub> and KMnO<sub>4</sub> mix solutions.</li> </ul>	Cadmium, Cd <sup>2+</sup>	Complexation with COOH and OH functional groups and coprecipitation, ion exchange, redox, electrostatic attraction, and cation- $\pi$ interaction.	pH: 5 Temperature : 25°C	120.77	NA	Adsorption performance of 45.4%- 66.2% after 3 regeneration cycles.	Heavy metal removal from wastewater	(Tan et al., 2022)
Highlights									

# Highlights

- Various synthesis and modification techniques of rice straw biochar are reviewed.
- Pyrolysis is the most established and prominent method to produce biochar.
- Acid-modified biochar is effective for metal ions and organic compounds removal.
- More understanding of the adsorption mechanism for other contaminants is needed.
- Recyclability and stability of biochar are essential for wastewater treatment.