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EXPLORATION OF THE OPTIMUM RICE HUSK BIOCHAR FOR ATRAZINE AND 2,4-D REMOVAL: DIFFERENT PYROLYSIS AND MODIFICATION CONDITIONS

Quach An BINH [1], *Nguyen Hong ANH* [1], *Vo Thi Diem KIEU* [1], *Nguyen Hai DANG* [1],
Nguyen Quy HAO [2], *Tra Van TUNG* [3]
1 *Dong Nai Technology University, Faculty of Applied Sciences–Health, Dong Nai, Vietnam*
2 *Vietnam National University Ho Chi Minh City (VNU-HCM), Key Laboratory of Advanced Waste Treatment Technology, Linh Trung Ward, Thu Duc District, Ho Chi Minh City, Vietnam*
3 *Vietnam National University Ho Chi Minh City (VNU-HCM), Institute for Environment and Resource, Ho Chi Minh City, Vietnam*
E-mail: quachanbinh@dntu.edu.vn

ABSTRACT

In this study, the best RHB (rice husk biochar) was investigated through the effect of pyrolysis synthesis processes and modifications. Five biochars were synthesized from rice husk waste materials at different pyrolysis temperatures (400 to 600 °C) in oxygen-limited conditions. The biochars were modified by acids to remove minerals on the surface area. The characteristics of the biochars were determined including surface morphology, specific surface area, and functional groups. The herbicide adsorption was accomplished by the batch equilibration method. The result indicated that the biochar that synthesized 500 °C for 6 h had the highest maximum adsorption capacity. The optimum RHB was biochar modified with HF acid. The optimum biochar had less or no minerals and it achieved abundant functional groups on the surface areas. The pore volume distributions in pore sizes of micropores and narrow mesopores played an important role to perform the uptake of the herbicides, they were in the range of 7.90 % and 59.26 %, respectively. The high-efficiency removals of atrazine and 2,4-D by optimum biochar were 82.70 % and 95.10 %, respectively. The rice husk biochar is a suitable adsorbent to remove herbicides from the aqueous environment.

Keywords: Adsorbent; Adsorption; Atrazine; Biochar; 2,4-D.

1 INTRODUCTION

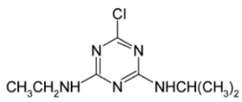
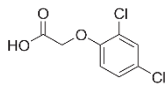
Pesticides were used widely to raise the agriculture yield, and product value [1,2]. As a result, pesticide residues appeared in surface water where these have harmful effects [3]. Atrazine is used in agriculture as a herbicide in order to control grass and broad–leaf weed. Moreover, it is also applied in airfields, parking lots, and industrial zones [4]. Atrazine is associated with causes of cancer, including that of lymphatic system and haematopoiesis [4]. 2,4-D is a herbicide that is widely used in agriculture as an agent for weed management. Its action is selective and it is a low-priced [5]. 2,4-D is a reason to cause the hepatotoxic and nephrotoxic to animal [6]. All herbicides are harmful to humans and the environment [4,6]. The physicochemical properties of herbicides are summarized in Table 1.

Thermochemical processes that produce biochar are slow pyrolysis, fast pyrolysis, and gasification [7]. But the yield of biochar synthesized from slow pyrolysis is higher than those of the fast pyrolysis or gasification [7]. Biomass contains compounds such as cellulose, hemicellulose, and lignin, and these compounds convert to biochar carbon matrix. However, the compounds convert to biochar at different temperature ranges. For instance, hemicellulose degrades in a range from 200 to 260 °C. Cellulose degradation occurs in a range from 240 to 350 °C, and lignin degradation occurs in a range from 280 to 500 °C. On the other hand, the original biomass has the amount of minerals that can affect biochar properties, the minerals are ash content after the burning process [8]. The ash can cap the pores of the biochar leading to a decrease in a specific surface area and the sorption of biochar. Therefore, it is very important to remove ash from biochar when biochar is used in adsorption. In order to decrease the amount of ash, the biomass could be washed with acid after pyrolysis [9].

Biochar is an adsorbent that is widely used in adsorption techniques. It contains a rich content of carbon after the pyrolysis process under oxygen-limited conditions. Many benefits of biochar properties are its good affinity and potential for adsorbing agrochemicals and pesticides [8, 10]. Several specific characteristics of biochar consist of excellent porosity, great specific surface area, and functional groups [11]. Biomass is abundant and low-cost [12]. Hence, if they are synthesised into adsorbents, they can be valuable materials. Rice husk is a waste material occurring in large quantities, the density of rice husk is 83–125 $kg.m^{-3}$; the amount of water that can penetrate in rice husk ranges from 5 % to 16 % of unit weights [13]. The rice husk components contain approximately 40 % cellulose, 30 % lignin group, 20 % silica, and other minerals including calcium, copper, iron, potassium, magnesium, manganese, sodium, phosphorus, and zinc [13,14]. There are many reports related to biochar (corn straw and switchgrass biochar) used in the removal of 2,4-D and atrazine [15,16], however, some of them do not report high removal efficiency, therefore, finding good biochar is necessary for application in the herbicide removal.

The aim of this study was to explore the effect of pyrolysis conditions on the mass loss of the biochar through the pyrolysis temperature. The pyrolysis process of biochar was performed under oxygen-limited conditions and was then modified by acids to remove the minerals. The methods and measurements including SEM (scanning electron microscope), BET (Brunauer-Emmett-Teller), FT-IR (Fourier-transform infrared spectroscopy), and the contact angle method were used to identify the characteristics of biochar. Comparisons are made between the atrazine adsorption capacities of the biochar modifications and to select the optimum biochar which is the highest adsorption capacity. The removal efficiencies of herbicides including atrazine, 2,4-D by optimum rice husk biochar were achieved.

Table 1. *The physicochemical properties of herbicides*

Herbicides	Molecular weight	Water solubility	$logK_{ow}$	Chemical structure	References
Atrazine	215.69	30 $mg.L^{-1}$	2.3		[17,18]
2,4-D	221.01	569 $mg.L^{-1}$	Not available		[19,20]

2 MATERIAL AND METHODS

2.1 Chemicals and materials

The rice husk biomass for biochar synthesis was gathered in Dong Nai province, Southern Vietnam. The 2,4-D (80 % w/v) was purchased from Tigicam company, Vietnam. Atrazine (80 % w/w) was provided from Sai Gon Plant Protection, Vietnam. HCl (37.00 %), HF (48.00 %), and H_2SO_4 (98.00 %) were purchased by Merck company, Germany.

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2.2 Preparation of adsorbents

Rice husk is approximately 3–5 mm in size and it is yellowish brown in colour. In order to remove the moisture that was obtained from the biomass, it was left in the sun for four days. The biomass was dried in the oven at 105 °C until a constant weight was gained. After removing the moisture, the sample was kept in a plastic bag. Approximately 30 g of biomass was inserted into the ceramic crucible and was pyrolysed in a furnace (Nabertherm, Germany), the heat in the furnace was raised gradually at 3 °C per minute [21]. To compare the adsorption capacity of the biochar under different burning conditions, the biochar was burned over 6 h and at different pyrolysis temperatures. All the pyrolysis processes were operated under oxygen-limited conditions. The lid was put on the ceramic crucible properly to avoid the outer oxygen disrupting the pyrolysis process [22].

The pristine biochars after the pyrolysis process were crushed, and sieved through a 0.8 mm sieve. The residual mineral on the surface of biochar was rinsed with acid (27 grams of biochar in 1 litre of acid 0.1 M) [9]. Next, the biochar was washed repeatedly with deionized water. The washing with acid was stopped, when the pH of the solution is neutral. Whatman filter paper 42 (retention: 2.5 μm) was used to diverge the biochar from the solution. The biochar was in a powder form after the drying process in the oven at 75 °C for 10 h [9].

2.3 Characterization of the biochar

The scanning electron microscope (LEO 1455 VP model, Carl Zeiss Microscopy GmbH, England) was operated to examine the surface of biochar. The specific surface area of biochar was verified by the BET method (TriStar II 3020, Micromeritics Instrument Corporation, USA). The functional groups of biochar were verified by the FT-IR method (Frontier, PerkinElmer, Germany). The hydrophilic characteristic of biochar was verified by the contact angle method (OCA 20, Dataphysics OCA GmbH, Germany).

2.4 Adsorption experiment

The batch adsorption method was carried out for the adsorption of biochar and herbicides. The dosage of RHB was 1.5 g.L^{-1} (0.15 g of biochar was added to 100 ml of herbicide). All experiments were performed by conical flasks and Shaker (MS-NOR-30/MS-NOR-3001). The conical flasks were agitated for equilibrium time at 120 rpm in the darkness. The herbicide solutions were collected during the experiment to analyse the residual concentration by UV–Vis spectrometer (Genesys 10S UV-Vis Thermo Scientific, USA). The wavelength to analyze atrazine, 2,4-D, were 229 nm [23], 230 nm, respectively. The maximum absorbance of 2,4-D was performed in triplicate from the scanning at a range of 200–600 nm and repeated triplicate with similar results (230 nm). The stock solution of 2,4-D (1000 mg.L^{-1}) was prepared from 1.25 ml (2,4-D, 80 % w/v). The stock solution of atrazine (100 mg.L^{-1}) was prepared from 125 mg (atrazine (80 % w/w). Two stock solutions were performed in a 1000 ml volume flask with DI (Deionized) water. The initial concentrations of atrazine to calculate the adsorption isotherm were from 10 to 25 mg.L^{-1}. The concentration using in the removal efficiency of atrazine and 2,4-D were 20 mg.L^{-1}.

The amounts of herbicides adsorbed on biochar at time t, qt (mg.g^{-1}) and at equilibrium, qe (mg.g^{-1}) were followed equations as below:

$$q_t = \frac{V\,(C_o - C_t)}{W} \qquad \textbf{\textit{(1)}}$$

$$q_e = \frac{V\,(C_o - C_e)}{W} \qquad \textbf{\textit{(2)}}$$

The percentage removal of herbicides are calculated using equation as below [5]:

$$\%\ \text{Removal} = \frac{100\,(C_o - C_e)}{C_o} \qquad \textbf{\textit{(3)}}$$

where C_o and C_e (mg/L) are concentrations of herbicides at initial and equilibrium, respectively; W (g) is the mass of dry biochar used; V (L) is the volume of the herbicide solutions [5,15].

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To evaluate the adsorption capacity of the herbicides on the RHB, Langmuir isotherm model was applied to calculate the adsorption experiment data.

Langmuir isotherms is shown as below:

$$q_e = \frac{Q_o\, K_L\, C_e}{1 + K_L\, C_e} \tag{4}$$

where Q_o (mg/g) is the maximum adsorption capacity; K_L (L/mg) is the Langmuir isotherm constant [15].

3 RESULTS AND DISCUSSION

3.1 Characterizations of the rice husk biochar

3.1.1 Effect of pyrolysis conditions on the mass loss of the biochar

The influence of the pyrolysis temperatures on the mass loss of the rice husk biochar are shown in Figure 1. In the pyrolysis process, the heating temperature is a factor that has a strong effect on the biochar yield. When increasing the temperature, the mass of the biochar decreased. At 100 to 200 °C, the mass of the biochar slightly decreased from 98.53 to 86.67 %. This was likely to be due to the loss of moisture content [24], this result agrees with previous experimental results [24]. At 300 °C, the percentage of the mass of the biochar decreased to 53.67 %, this temperature significantly influenced the loss of biochar. When the temperature was from 400 to 550 °C, the mass of the biochar decreased from 45.51 to 37.68 %. The mass of the biochar stabilized at a temperature of 600 °C (34.72 %). According to Demirbas, biomass consists of cellulose, hemicelluloses, water, lignin, simple sugars, extracts, lipids, proteins, starches, ash, hydrocarbons, and other compounds (2009) [25]. The decrease in mass is explained through the pyrolysis process, the biomass transformed into biochar, bio-oil, and syngas [8]. At high pyrolysis temperatures, the volatile material was transferred and released significantly, which changed the yield of the biochar [26]. Therefore, when the biomass is burned at high temperatures, the yield of the biochar decreased significantly.

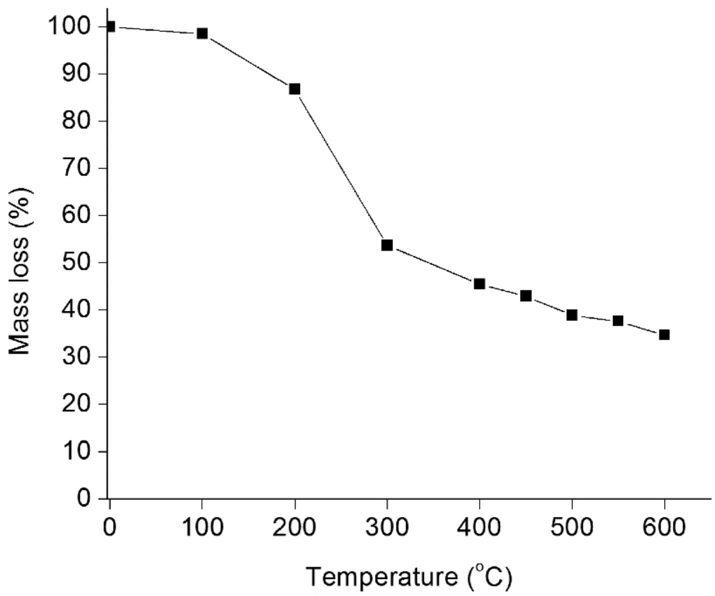

Figure 1. *Effect of the yield (%) of the mass loss of RHB by the pyrolysis temperatures in 6 h*

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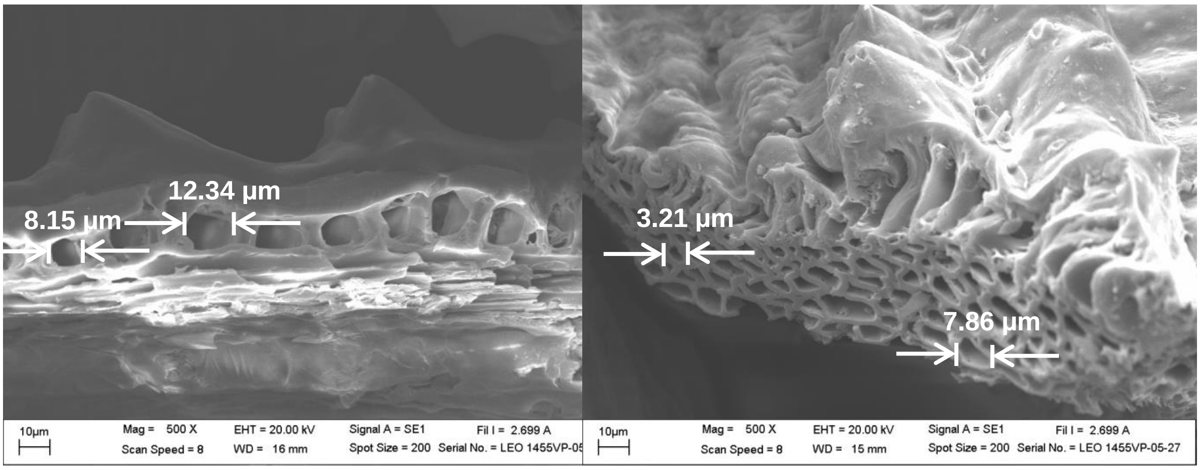
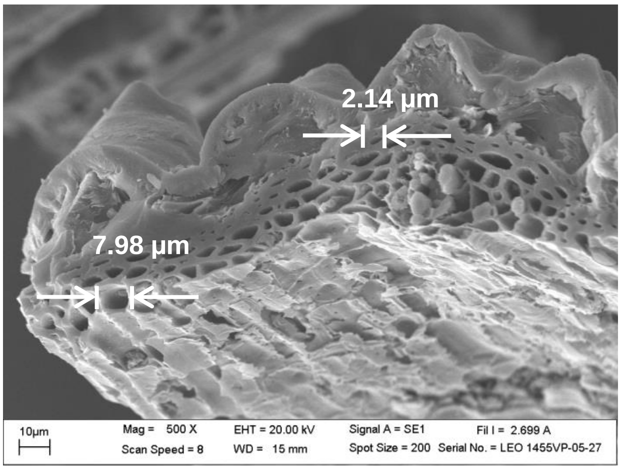
3.1.2 Surface morphology of rice husk biochars

The SEM pictures of different RHB (modification with HCl acid) are shown in Figure 2. When the pyrolysis temperature increased from 400 to 600 °C, the pore sizes of the biochar width tended to be narrow. The width range of RHB 400 °C was approximately 8.15–12.34 μm. This was considered in [27], when biochar formed pore openings. Whereas the pores in RHB 500 °C are various sizes. The small amount of volatile matter in the biochar was slowly lost, this formed the various pore sizes at 500 °C [27]. When biochar was burned at 600 °C, the total dissolution of small parts of the volatile matter that remained in the biochar was achieved. The RHB showed that the pores on the surface of the biochar are longitudinal in shape, which indicates that RHB can take up pollutants by a pore-filling mechanism.



(a) *(b)*



(c)

Figure 2. *SEM of RHB synthesised under different pyrolysis temperatures for 6 h (modification with HCl acid): (a) 400 °C, (b) 500 °C, (c) 600 °C*

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3.2 Comparison of the RHB by the Q_o (maximum adsorption capacity)

The results of the pyrolysis temperature affected on the Q_o of RHB are shown in Figure 3. The Q_o increased from 10.10 to 14.00 mg.g^{-1}, when biochar was synthesized from 400 to 500 °C for 6 h (Figure 3). This explains that the increasing of the pyrolysis temperature due to enhancement of the specific surface area (SSA) [26]. The adsorption ability of biochar depended on the total pore volume (TPV) and SSA significantly [28]. However, the pyrolysis process was performed from 550 to 600 °C in 6 h, the Q_o of biochar decreased from 11.20 to 9.50 mg.g^{-1}. Probably, at 550 to 600 °C, the SSA of biochar could decrease due to the high temperature leading to the change in form of the pores of the biochar [8]. This caused the reduction in the Q_o of RHB that synthesized at 550 to 600 °C in 6 h. High temperatures and prolonged holding time could cause a decrease in the SSA and Q_o [8].

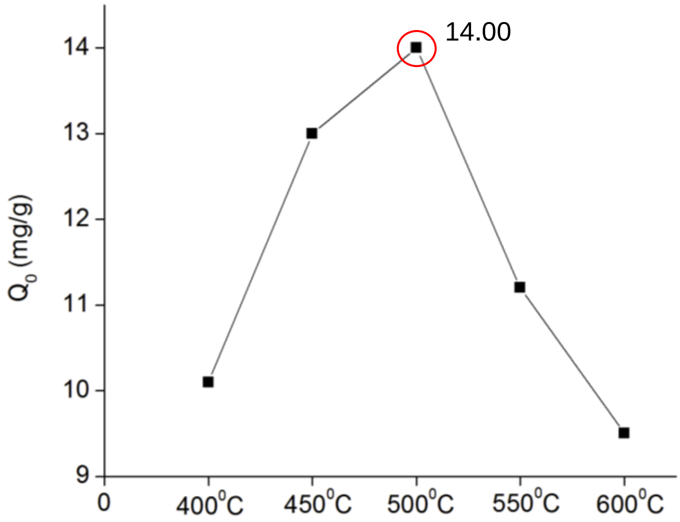

Figure 3. *The effect of pyrolysis temperatures for 6 h on the Q_o*
(dosage of biochar: 1.5 g.L^{-1}, [Atz]: 10-25 mg.L^{-1}, equilibration time: 24 h)

3.3 Comparison of the adsorption capacity of RHB 500 °C - 6 h - modified with many types of acid

The adsorption capacity of non-modified and modified RHB (acid modification) is shown in Figure 4. The results indicate that the capacities of RHB to absorb atrazine were higher if the biochars were modified with acid. The minerals blocked the pores of the biochar, impeding the transfer of atrazine into the pores. The adsorption capacity of RHB modified by HF acid was observed to be the highest. This is clarified by the ash composite of the biochar. The Si element was 87.00 % and a main component of ash in rice husk biochar, the residual components were Ca (2.0 %), P (0.9 %) and K (9.0 %) [29]. The Si ash of RHB was significantly removed by HF modification, this reports that the percentages of Si ash of RHB that synthesized at 450 °C and 600 °C were 80.00 % and 85.64 %, respectively [30]. The removal of Si from RHB by HF acid was due to HF reacting to Si creating SiF4. HF acid can also react with K on the surface of the biochar [31]. HF acid is able to corrode glass, as the fluoride anions can react with silicon molecules which exist in glass thus damaging glass [32]. Therefore, the main ash of RHB including Si and K was removed by HF acid, which brought about the highest adsorption capacity for biochar.

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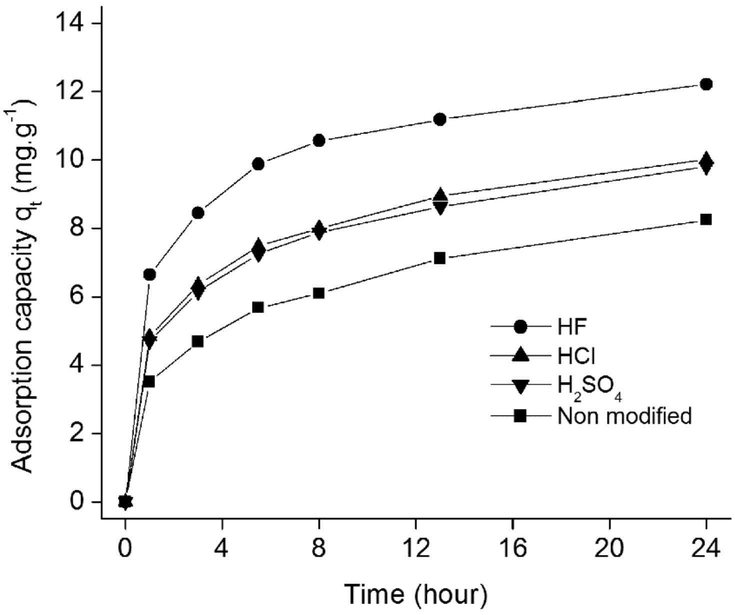

Figure 4. *The adsorption capacity (q_t) of RHB 500 °C – 6 h (acid-modified) adsorbed atrazine ([Atz]: 25 mg.L^{-1}, adsorption time: 24 h)*

3.4 Characterization of the optimum RHB

The SEM (scanning electron microscope) picture of acid-modified biochar is shown in Figure 5. The biochar with acid modifications presented fewer or no minerals, allowing higher adsorption capacity.

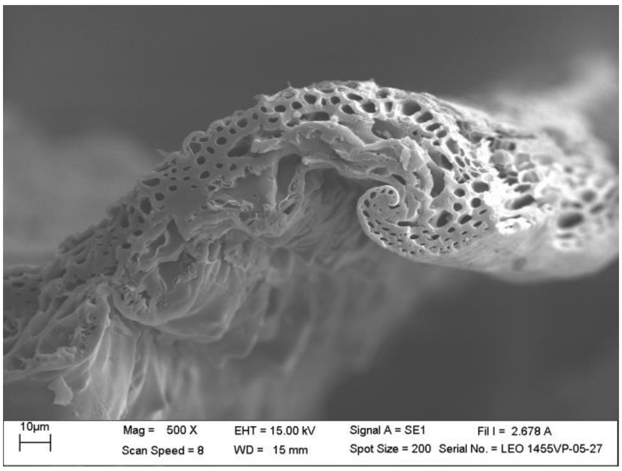

Figure 5. *SEM picture of RHB 500 °C - 6 h modified with 0.1 M HF acid*

The specific surface area (SSA) and total pore volume (TPV) of the RHB were 153.27 m^2.g^{-1} and 0.055 cm^3.g^{-1}, respectively. If the large specific surface area exists on the surface of the biochar, it has more interfaces for pollutant adsorption [15]. The pore size of the biochar played an important role in pore-filling adsorption. The pore volume distributions (%) in pore sizes of micropores (< 2 nm) and narrow mesopores (2-20 nm) were in the range of 7.90 % and 59.26 %, respectively. The pore size of the biochar is very important in performing the uptake

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of the adsorbate [28]. The contact angle method indicated that the surface of biochar was totally wet with water ($\theta < 30$ °), the pore of RHB can penetrate the water and pollutants [33].

Figure 6 shows the FT-IR analysis of the optimum RHB. The main functional groups of the RHB comprised the ketone, carbonyl, and aromatic organic molecules and are unsaturated hydrocarbons. The hydroxyl group is an abundant molecule on the surface of RHB and can bring about H-bonding interaction between RHB and pollutants [34]. In addition, the aromatic group of the RHB can generate the π-π EDA interaction [34] and the alkyl group can engender the hydrophobic bonding [35].

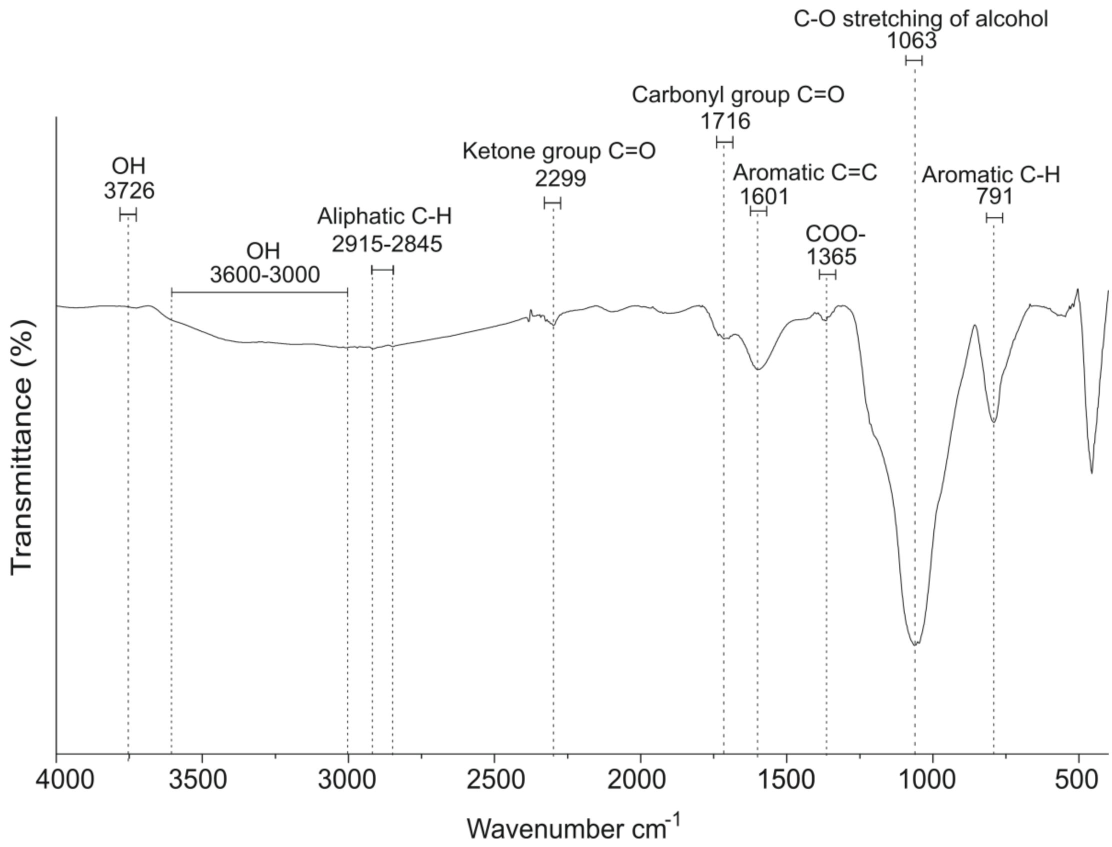

Figure 6. *The FT-IR spectrum analysis of the optimum RHB*

Table 2. *The FT-IR analysis result of the optimum RHB*

Wavenumber (cm^{-1})	**Assigned to the type of vibration**	**The functional group**	**References**
791	C-H	Aromatic C-H	[36]
1063	C-O	C-O stretching of alcohol	[37]
1601	C=C	Aromatic hydrocarbon	[37]
1716	C=O	Carbonyl group	[34]
2299	C=O	Ketone group	[38]
2915-2845	C-H	Aliphatic C-H	[35]
3600-3000	O-H	Alcohol, phenol, carboxylic acid	[36]

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3.5 The removal efficiency of optimum RHB

The removal efficiency of herbicides by the optimum RHB are shown in Figure 7. The removal of atrazine, 2,4-D were removed at a high percentage and were 82.70 and 95.10 %, respectively. The removal efficiency of atrazine (82.70 %) in our study is higher than those (12.00 %) of Tan et al.'s study, 2016 (the atrazine concentration: 10 mg.L^{-1}, the dose of corn straw biochar: 33.3 g.L^{-1}) [15]. For the removal efficiency of 2,4-D, this is similar to the study results of Essandoh et al., 2017 (90 % removal, the 2,4-D: 40 mg L^{-1}, the dose of switchgrass biochar: 1.0 g.L^{-1}) [16]. The removals of herbicides are related to the adsorption mechanism between biochar and herbicides. Based on the SEM, BET, and FT-IR of the optimum RHB and molecular structure of atrazine and 2,4-D, the suggestion of the adsorption mechanism is the pore-filling, electrostatic, hydrophobic bonding, H-bonding, π-π EDA interactions [12].

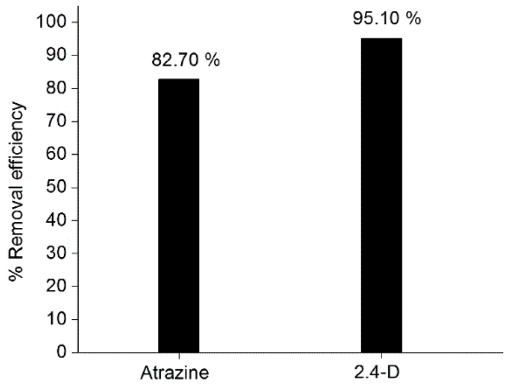

Figure 7. *The removal efficiency of herbicides by optimum RHB*
(dosage of biochar: 1.5 g.L^{-1}, [Atz] = [2,4-D]: 20 mg.L^{-1}, adsorption time: 24 h)

4 CONCLUSION

This study explored the best rice husk biochar from different pyrolysis conditions and modifications. When the biomass is burned at high temperatures, the yields of the biochar decreased significantly. The optimum biochar from different pyrolysis conditions is biochar that was synthesized at 500 °C for 6 h. The optimum biochar was observed when it was modified with HF acid. The optimum biochar had less or no minerals, and it achieved the abundant function groups on the surface areas. The pore volume distributions (%) in pore sizes of micropores and narrow mesopores were in the range of 7.90 % and 59.26 %, respectively, and were an essential factor to adsorb the herbicides. The removal efficiency of the optimum biochar for atrazine and 2,4-D is very high in the range of 82.70 to 95.10 %. From the results of this study, the rice husk biochar is an advantageous adsorbent to remove herbicides from the aqueous environment.

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