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Physicochemical Properties of Activated Carbons Produced from Coffee Waste and Empty Fruit Bunch by Chemical Activation Method

Vilaysit Thithai [1] , **Xuanjun Jin** [1] , **Muhammed Ajaz Ahmed** [2] **and Joon-Weon Choi** [1,2,*]

[1] Graduate School of International Agricultural Technology, Department of Green Ecosystem Engineering, Seoul National University, Pyeongchang 25354, Gangwon-do, Korea; vilaysit@snu.ac.kr (V.T.); xj.jin@snu.ac.kr (X.J.)

[2] Institute of Green-Bio Science and Technology, Seoul National University, Pyeongchang 25354, Gangwon-do, Korea; m.ajaz@snu.ac.kr

[*] Correspondence: cjw@snu.ac.kr; Tel.: +82-33-339-5840; Fax: +82-33-339-5830

Abstract: In this study, coffee waste (CW) and empty fruit bunches (EFB) were employed as precursors for the production of activated carbons by a chemical activation method. KOH, $ZnCl_2$, and H_3PO_4 were used as activating agents along with their three mixing ratios of 1:0, 1:1, 1:3, *w/w,* and carbonization temperatures of 600 °C, 700 °C, and 800 °C were used to prepare these activated carbons. The highest yields of produced activated carbons were observed at 600 °C with a value of 45.20% for coffee waste and 48.20% for empty fruit bunch, with a 1:3 *w/w* (H_3PO_4) ratio. However, the maximum specific surface area was 3068 m^2 g^{-1}, and 2147 m^2 g^{-1} obtained at 800 °C for coffee waste and empty fruit bunch activated carbons, respectively. The surface features of these products exhibited acute morphological changes, as were clearly noticed via SEM studies. Moreover, in the Van Krevelen diagram, it was also observed that both the H/C and O/C ratios were dramatically decreased to 0.0019 and 0.0759, and 0.0066 and 0.1659 for coffee waste and empty fruit bunch at 800 °C with a (1:3) potassium hydroxide and zinc chloride ratio, respectively, and this similar phenomenon was also supported by a thermal gravimetric analysis. All these results, together with the specific characteristics of the products, suggest that this scheme can be an effective strategy for the activated carbon production from such residues.

Keywords: coffee waste; empty fruit bunch; activated carbon; chemical activation; activating agent; specific surface area; pore volume

1. Introduction

Coffee is one of the most common agricultural commodities in many parts of the world, and it is currently one of the most widely consumed beverages [1]. This is cultivated in almost more than 70 countries, yielding around 16 billion pounds of coffee beans per annum [2]. Coffee grounds, commonly known as coffee waste (CW), are the major residue found downstream of the coffee processing industries, mainly generated during the extraction of the beverage from coffee powder with hot water. Such wastes, according to one study, can even amount to up to 6 million tons per annum, posing thus a huge burden on the global ecosystem [3].

In conjunction with this waste, empty fruit bunch is also an important waste product generated as a leftover from oil extraction processes found abundantly in the Southeast Asian region with a total annual production of 37 million tons [4]. Generally, these empty fruit bunches (EFB) are approximately 24 wt% of the total solid waste produced during the production of the oil extraction process [5]. However, this byproduct material is usually being utilized as an organic fertilizer for mushroom production and heating purposes [6,7]. These biomass wastes can possibly be employed for the generation of bio-oils, biogas, bioethanol, activated carbon, and even in the production of commodity chemicals [8].

Among these, activated carbon being more diverse in its applications could be more suited for such substrates. This material possesses a porous structure with improved characteristics favoring enhanced adsorption of different compounds. Such activated carbons can be produced from various types of agricultural byproducts such as corn cob [9], corn stalk [10], rice straw [11], palm kernel shells [12], coffee husk [13], cassava peel [14], coconut shell [15], durian shell [16], pomegranate seeds [17] and many others.

In general, there are two methods for activation, which are commonly known as physical activation and chemical activation. For the physical activation, the feedstock is firstly carbonized with the help of steam and/or carbon dioxide at higher temperatures. Nevertheless, such physical activation methods produce an activated carbon with a low specific surface area and fewer pore volumes compared to the chemical activation methods [18]. However, on the other hand, for chemical activation, the feedstock is impregnated with activating agents followed by carbonization at temperatures ranging from 600–900 °C under nitrogen atmosphere [19,20]. For such processes, the most commonly adapted chemicals include KOH, $ZnCl_2$, NaOH, K_2CO_3, and H_3PO_4. Under such processes, during the impregnation stage, activating agents are transported into the substrate cell walls forming effective cross-links between them, thus ensuring the formation of more pores upon their release [21].

Additionally, such type of chemical activation method has demonstrated more benefits over physical activation due to its acceptable performance even at lower temperatures with high yields and resulting in a high specific surface area end product. At the same time, the main challenge in the production of activated carbon is the development of an economically justified method to obtain products with given surface properties using a low-cost feedstock [22–24]. Therefore, in this study, we employed a chemical activation method for the production of activated carbons from coffee wastes and empty fruit bunches. These products were also studied for their yield, physical characteristics such as surface morphology, surface area, pore size, and pore volume, together with the van Krevelen diagram.

2. Materials and Methods

2.1. Biomass Preparation

Coffee waste (CW) was obtained from the coffee shop in the Pyeongchang district, in the Gangwon province of South Korea, and the empty fruit bunch (EFB) was provided from the Malaysian company, as reported in one of our previous studies [25]. Both the biomasses were first subjected to air-drying and then ground in a grinding machine (FRITSCH, PULVERISETTE 19, Idar-Oberstein, Germany) and were finally sieved to a particle size of 0.5 mm mesh size. These were then washed thoroughly with deionized water to remove any dirt and mineral contents and then were dried in an oven at 50 °C till a constant weight was obtained. All the chemicals used in this study, such as potassium hydroxide (KOH $\geq$ 85% purity), zinc chloride ($ZnCl_2 \geq$ 97% purity), and phosphoric acid ($H_3PO_4 \geq$ 99.0% purity), were bought from Sigma-Aldrich and used without any modification.

2.2. Compositional Analysis of Coffee Waste and Empty Fruit Bunch

An elemental analysis (CHNS/O) of the biomass feedstock was done by analyzing samples on a CHNS-932 instrument (LECO Corp., USA) [26]. The component analysis, such as holocellulose (consisting of cellulose and hemicellulose), lignin, and ash, was conducted according to the National Renewable Energy Laboratory (NREL) two-step standard procedure [27]. For the thermal degradation analysis and Thermogravimetric analysis (TGA), a Mettler-Toledo AG Instrument (Switzerland) was used. For this analysis, the specified sample weight was added to an alumina crucible and heated from 25 °C to 800 °C under an inert atmosphere (flow rate of 50 mL min^{-1}) at a constant heating rate of 10 °C min^{-1}, and the corresponding results have been presented in Table 1. For the determination of inorganic compounds, inductively coupled plasma emission spectroscopy

(ICP-ES) was used employing an ICPS-1000IV instrument (Shimadzu, Japan). To this end, firstly, around 0.5 g of biomass was digested with 10 mL of an acid mixture of HNO_3: HCl: H_2O_2 (8:1:1, *v/v*) in a Microwave Reaction System SOlV (Anton Parr, AT/Multiwave Pr, Graz, Austria). After the digestion, the sample was diluted with deionized water to 50 mL and then filtered with a filter paper (Whatman No.42). The filtrated sample was collected and analyzed using ICP-ES, and the results have been shown in Table 2 for coffee waste (CW) and empty fruit bunch (EFB), respectively.

Table 1. Characterization of physicochemical properties of feedstock.

Elemental Analysis (wt%)	Coffee Waste	Empty Fruit Bunch
Carbon	51.5	45.8
Hydrogen	8.1	6.6
Nitrogen	2.0	0.6
Sulfur	0.5	0.5
Oxygen [a]	38.0	46.6
Component analysis (wt%) [b]		
Holocellulose	44.5	73.1
Lignin	19.5	22.1
Extractive	18.9	3.0
Ash	1.3	5.4
Proximate analysis (wt%)		
Volatile matter	83.6	74.2
Fixed carbon	16.3	25.7

[a] By difference in weight; [b] Dry basis.

Table 2. Determination of the inorganic content of coffee waste and empty fruit bunch.

Inorganic Compound Analysis (mg L^{-1})	Coffee Waste	Empty Fruit Bunch
Aluminum	0.387	10.364
Calcium	13.405	21.710
Iron	0.682	18.266
Magnesium	16.661	8.006
Potassium	4.859	7.744
Copper	5.927	4.690
Silicon	1.940	23.483

2.3. Preparation for Chemical Activation from Coffee Waste and Empty Fruit Bunch

Chemical activation of both the coffee waste (CW) and empty fruit bunch (EFB) was performed by using three different types of activating agents (KOH, $ZnCl_2$, and H_3PO_4) along with their mixing ratios of 1:0, 1:1, and 1:3, *w/w* (feedstock: activating agent) at the different carbonization temperatures of 600 °C, 700 °C and 800 °C [28]. For this process, approximately 15 g of biomass feedstock was mixed with the specified amount of the activating agent and finally was loaded into the stainless-steel reactors. These reactors were then initially purged with nitrogen gas for around 10 min and finally moved into the furnace where a constant flow of nitrogen gas was maintained, and the sample was carbonized for about 1 h. After the carbonization, reactors were taken out from the furnace and cooled down to room temperature at ambient conditions. This produced activated carbon was taken out and washed completely with 1 M HCl solution, followed by an additional washing of distilled water to ensure complete neutralization (pH conformation). Thereafter, the washed activated carbons were dried in the hot-air oven at 105 °C for 24 h. The chemical activation was performed in triplicate, and the produced activated carbons of CW and EFB were labeled as CWAC, CWACK, CWACZ and CWACP and EFBAC, EFBACK, EFBACZ, and EFBACP (only CWAC and EFBAC represent controls and with K, Z, and P symbols represent activated with KOH, $ZnCl_2$, and H_3PO_4, respectively). The

yields of activated carbon were calculated by the following equation. Nevertheless, the yields of produced activated carbon were presented in Figures 1 and 2.

$$\text{Yield (\%)} = \frac{\text{Mass of activated carbon (g)}}{\text{Mass of feedstock (g)}} \times 100$$
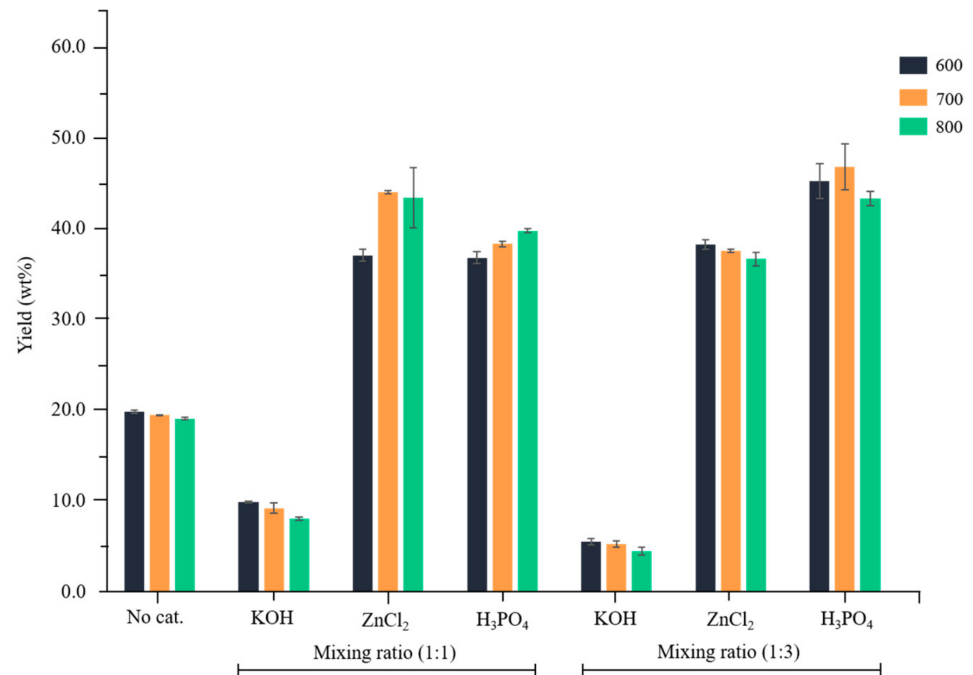

Figure 1. Comparison of yields of coffee waste activated carbon (CWAC) prepared by different temperatures, activating agents and mixing ratio of activating agent of 1:1 and 1:3, w/w.
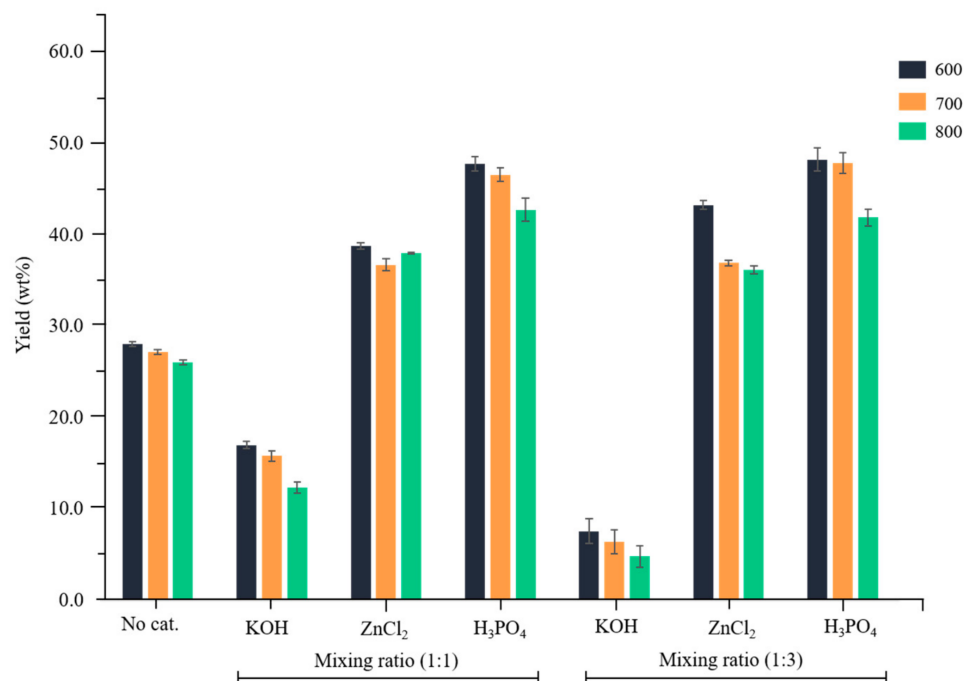

Figure 2. Comparison of yields of empty fruit bunch activated carbon (EFBAC) prepared by different temperatures, activating agents and mixing ratio of activating agent of 1:1 and 1:3, w/w.

2.4. Thermal Stability and Van Krevelen Diagram of Produced Activated Carbons

The elemental analysis (C, H, N, and O) for both coffee waste activated carbon (CWAC) and empty fruit bunch activated carbon (EFBAC) were determined using the same method as described in Section 2.2 and the analysis results have been reported in Table 3. Keeping in view the above analyses, a Van Krevelen diagram has also been drawn to study the post-activation changes in the biomass substrates and has been delineated in Figure 3. For thermal degradation, the behaviors of CWAC and EFBAC were conducted by using the same method with the feedstock as mentioned above and the results have been presented in Table 4 and Figure 4, accordingly.

Table 3. Determination of elemental composition of activated carbons.

Sample	Properties (wt%)	Temp (°C)	Activating Agents and Mixing Ratios						
			No Act [a]	KOH		ZnCl$_2$		H$_3$PO$_4$	
			1:0	1:1	1:3	1:1	1:3	1:1	1:3
CWAC	Carbon	600	78.4	72.0	78.1	79.1	85.9	70.4	55.7
		700	79.1	79.4	88.3	73.2	85.3	63.3	49.1
		800	79.8	85.6	92.7	70.7	82.1	59.8	46.3
	Hydrogen	600	1.8	0.9	1.1	1.5	1.4	2.0	1.9
		700	1.1	0.4	0.4	0.9	1.1	1.7	1.5
		800	0.7	0.3	0.2	0.7	0.8	1.5	1.3
	Nitrogen	600	3.5	2.1	0.3	3.1	2.8	2.5	2.3
		700	3.6	0.8	0.2	3.1	3.4	2.8	2.7
		800	3.5	0.4	0.1	2.8	3.4	2.7	2.5
	Oxygen [b]	600	16.3	25.0	20.5	16.4	9.8	25.1	40.1
		700	16.3	19.5	11.0	22.8	10.2	32.2	46.7
		800	15.9	13.7	7.0	25.8	13.7	36.0	50.0
EFBAC	Carbon	600	68.5	67.0	66.3	78.1	77.6	62.3	63.0
		700	74.1	72.8	73.0	75.9	85.8	55.5	51.7
		800	73.3	74.0	79.1	76.3	84.3	55.1	54.7
	Hydrogen	600		0.8	0.9	1.2	1.2	1.4	1.4
		700	0.9	0.4	0.5	0.8	0.9	1.1	1.1
		800	0.5	0.3	0.3	0.6	0.6	1.0	0.8
	Nitrogen	600	0.8	0.7	0.4	1.1	0.9	0.8	0.5
		700	0.7	0.5	0.3	1.0	1.2	0.8	0.7
		800	0.8	0.5	0.3	1.1	1.2	0.8	0.9
	Oxygen [b]	600	29.3	31.5	32.4	19.7	20.4	35.5	35.1
		700	24.2	26.3	26.1	22.2	12.1	42.6	46.5
		800	25.3	25.2	20.2	22.1	14.0	43.1	43.6

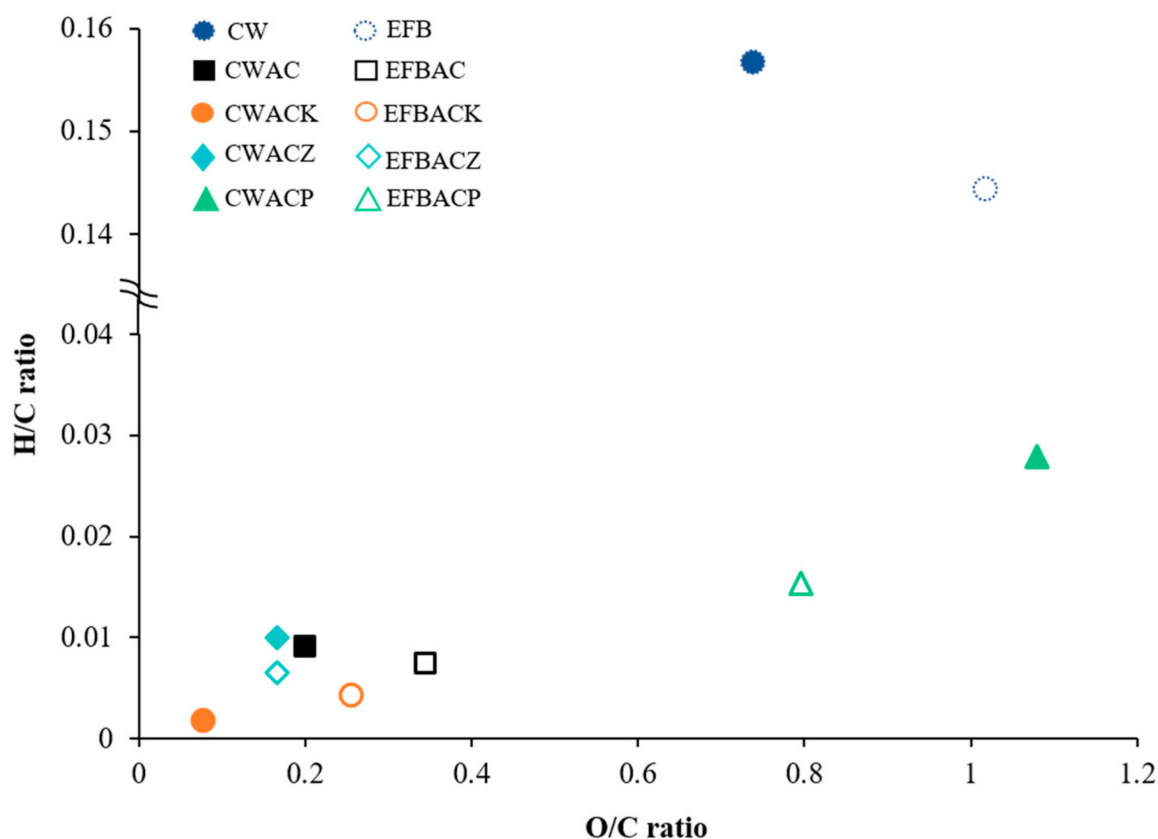[a] Non-activating agent; [b] by difference in weight.

Figure 3. Van Krevelen diagram of feedstock and activated carbons prepared with various activating agents and carbonization temperatures.

Table 4. Thermal degradation analysis of activated carbons.

| Sample	Properties (wt%)	Temp (°C)	Activating Agents and Mixing Ratios						
			No Act *	KOH		ZnCl$_2$		H$_3$PO$_4$	
			1:0	1:1	1:3	1:1	1:3	1:1	1:3
CWAC	Volatile matter	600	16.9	29.3	26.6	19.6	20.1	25.0	29.9
		700	12.1	23.7	42.5	27.2	20.3	19.5	22.2
		800	14.4	16.4	30.7	27.3	20.0	20.2	22.4
	Fixed carbon	600	83.1	70.7	73.4	80.4	79.9	75.0	70.1
		700	87.9	76.2	57.5	72.8	79.8	80.5	77.8
		800	85.6	83.5	63.3	72.7	79.9	79.8	77.6
EFBAC	Volatile matter	600	16.6	25.0	30.6	14.4	17.4	16.0	16.3
		700	13.0	16.9	24.7	13.5	9.0	14.0	13.7
		800	11.2	17.7	23.0	13.9	9.4	13.0	11.0
	Fixed carbon	600	83.4	75.0	69.4	85.6	82.6	84.0	83.7
		700	87.0	83.1	75.2	86.5	91.0	86.0	86.3
		800	88.8	82.2	77.0	86.1	90.6	87.0	89.0

* Non-activating agent.
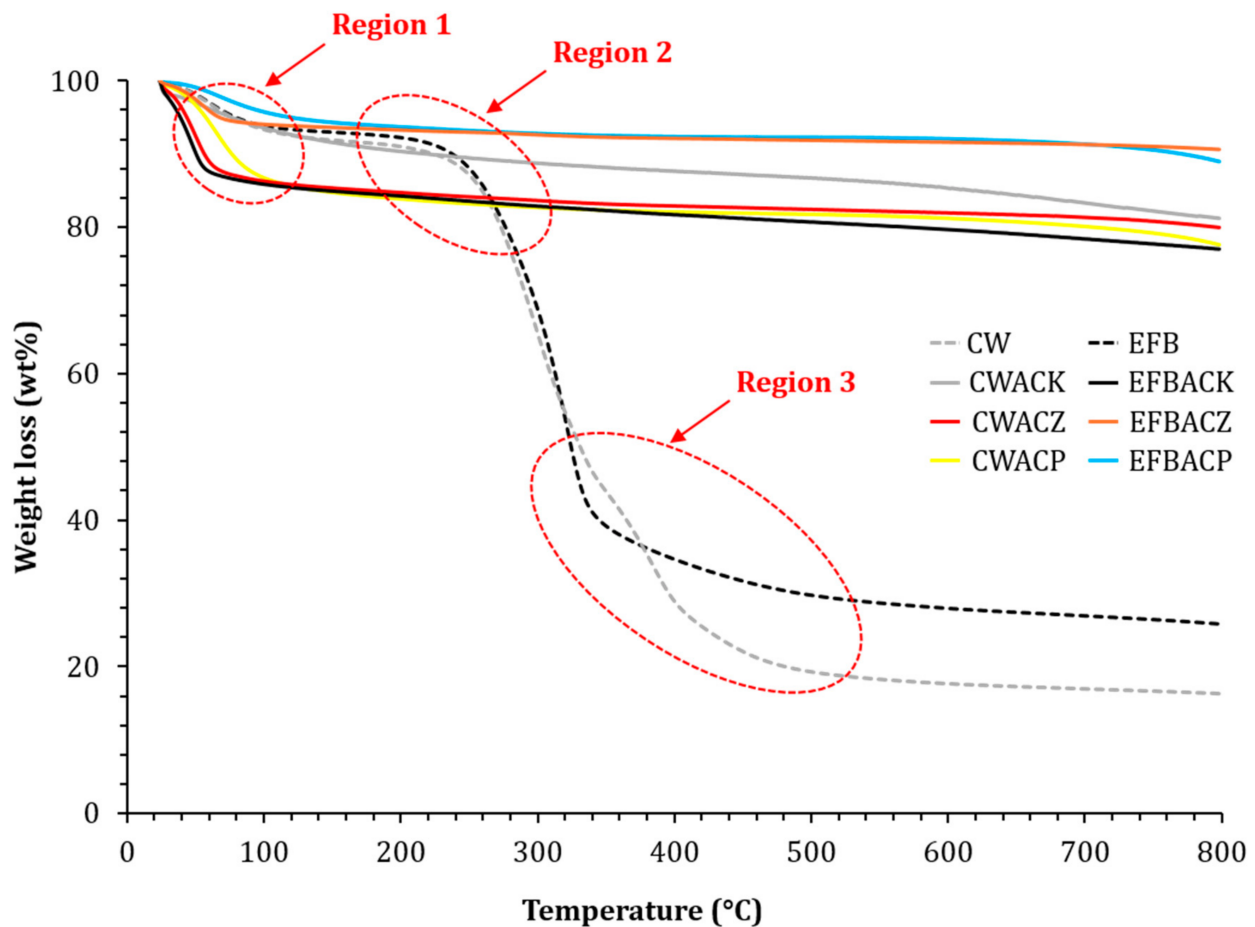
Figure 4. Thermal degradation for biomass feedstock and activated carbons.

2.5. Surface Features of Produced Activated Carbons

　　The surface features of all the produced activated carbons were studied by using field-emission scanning electronic microscopy (FESEM), using an AURIGA instrument (Carl Zeiss, Germany). For the surface area determination of CWAC and EFBAC, a Brunauer-Emmett-Teller (BET) method was used to evaluate the specific surface area from liquid nitrogen gas adsorption. The Barrett-Joyner-Halenda (BJH) method was used for pore size and average diameter characterization using adsorption branch, and the t-plot method was applied for evaluation of micropore structure by using a BELSORP-max instrument (Micro-tracBEL Corp, Japan) with a nitrogen adsorption-desorption isotherm at 77 K (-196 °C). For the gas adsorption measurements, the activated carbons were degassed at a temperature of 350 °C for 3 h, within the vacuum conditions aimed to improve the surface functions and remove the moisture contents from the surface of activated carbon. After degassing, the nitrogen gas was purged into sample cells before moving them into the instrument. The corresponding results have been reported in Figures 5 and 6.
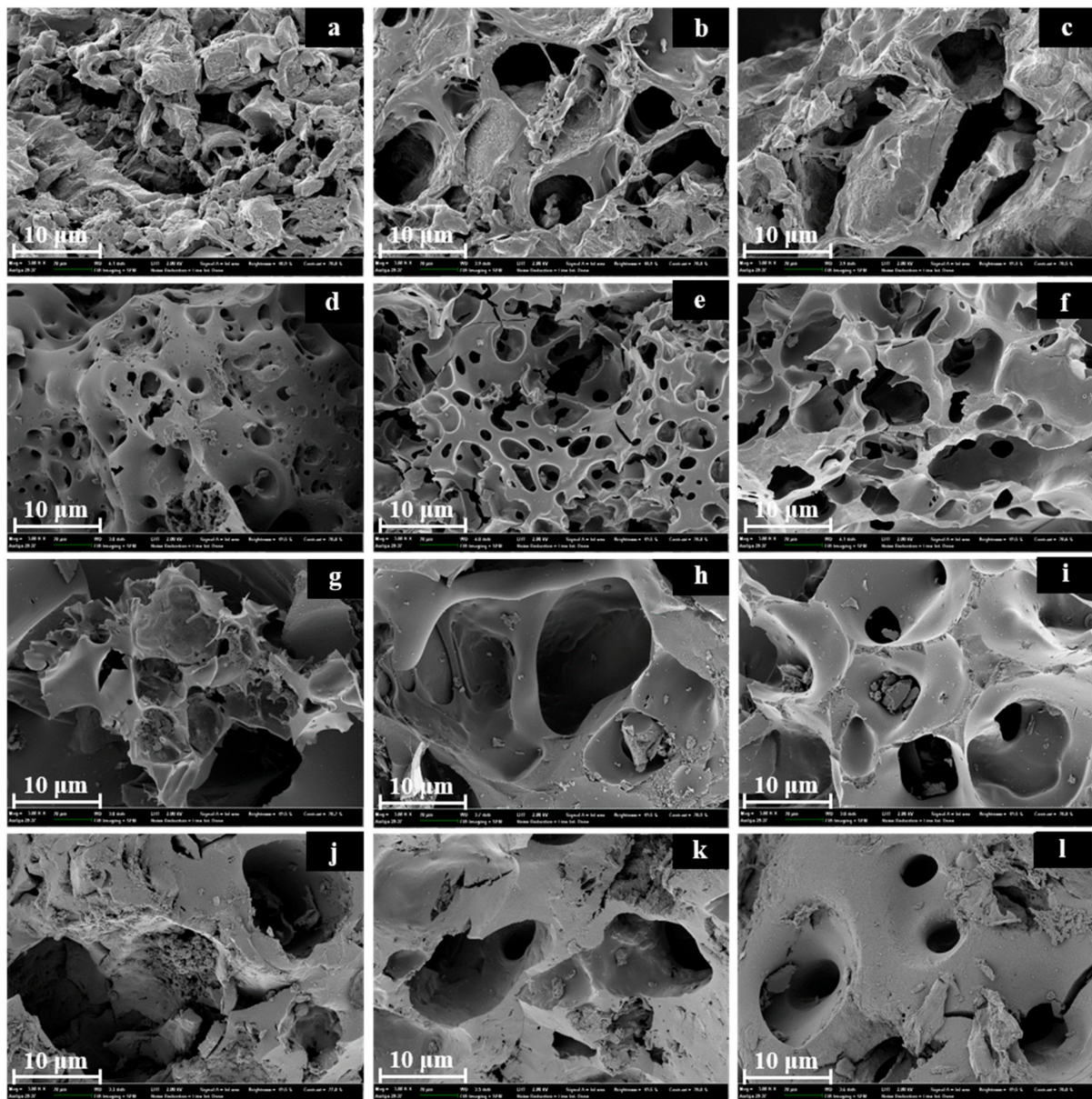
Figure 5. SEM image of coffee waste activated carbon prepared at different temperatures 600 °C, 700 °C and 800 °C. (**a**–**c**); CWAC, (**d**–**f**); CWACK, (**g**–**i**); CWACZ, and (**j**–**l**); CWACP, respectively (the SEM image of activated carbon prepared using a mixing ratio of activating agent of 1:1 is not included in this figure).

Figure 6. SEM image of empty fruit bunch activated carbon prepared at different temperatures 600 °C, 700 °C and 800 °C. (**a**–**c**); EFBAC, (**d**–**f**); EFBACK, (**g**–**i**); EFBACZ, and (**j**–**l**); EFBACP, respectively (the SEM image of activated carbon prepared using a mixing ratio of activating agent of 1:1 is not included in this figure).
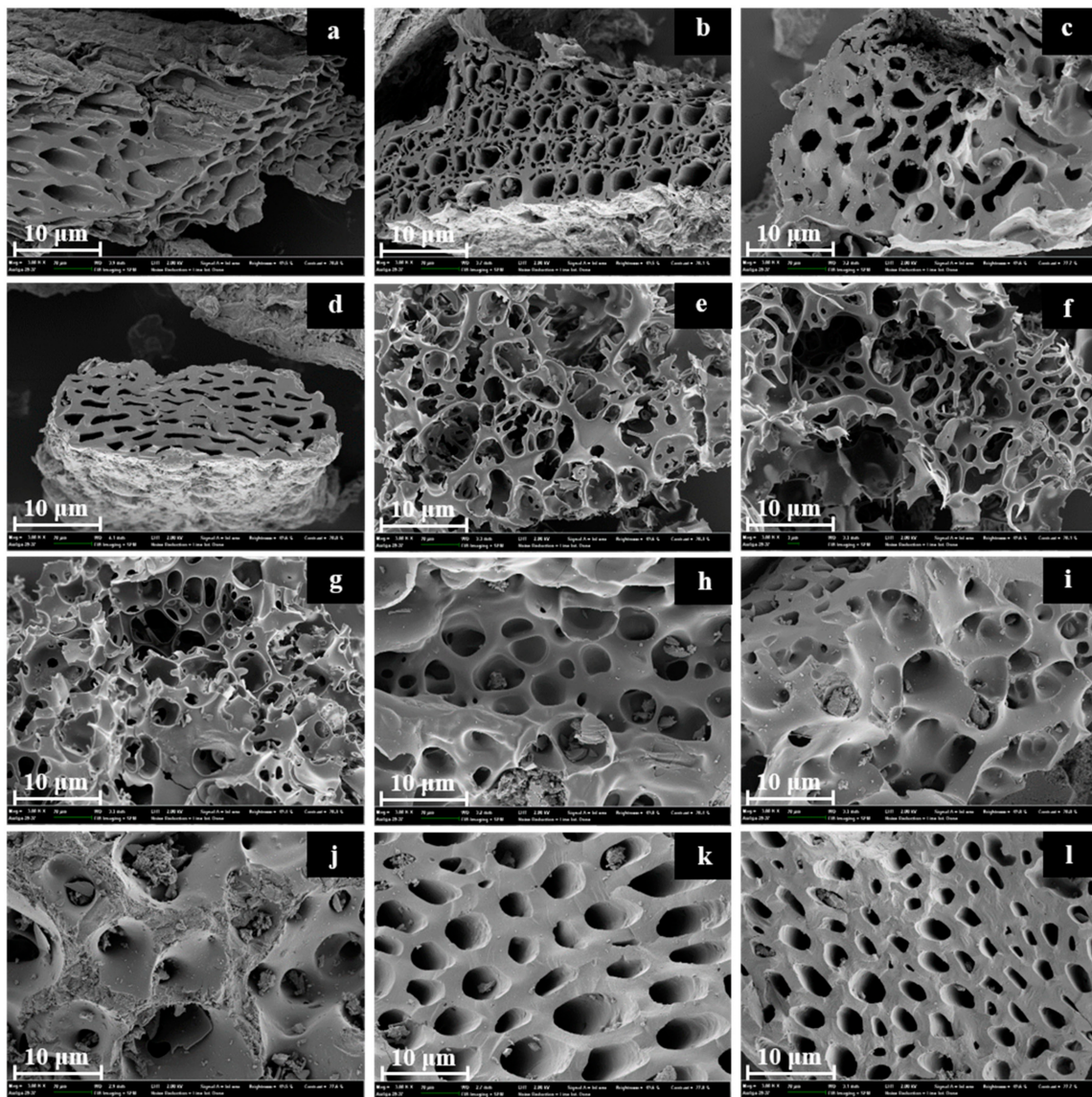
3. Results and Discussion

3.1. Yields of Activated Carbon Prepared by Chemical Activation

The yields of coffee waste and empty fruit bunch activated carbons prepared with different activating agents, and carbonization temperatures have been presented in Figures 1 and 2, respectively. Compared with the control, it can be observed that the yields of the empty fruit bunch activated carbon (EFBAC) were higher than the coffee waste activated carbon (CWAC). The yields of coffee waste activated carbon produced without any activating agent were 19.8 wt%, 19.4 wt%, and 19.1 wt%. At the same time, the yields of empty fruit bunch activated carbon were 28.1 wt%, 27.2 wt%, and 26.1 wt% for 600 °C, 700 °C, and 800 °C, respectively. Meanwhile, the yields of CWACK and EFBACK were dramatically decreased by increasing the ratio of KOH. Thus, KOH had an adverse impact on the production yield of activated carbon in our case, as the rate of weight loss was high primarily due to the initial large amount of volatiles that was easily released with increasing both the activating agent ratio and carbonization temperatures. In our previous study related to the carbonization of corn stover with alkaline hydroxide, chloride, and acid, we found

a similar result for KOH chemical activation [28]. The CWACZ, CWACP, EFBACZ, and EFBACP show that yields slightly increased by increasing the activating agent ratio and carbonization temperatures. As reported in one previous study, $ZnCl_2$ and H_3PO_4 are dehydrating agents that influence the pyrolytic decomposition and inhibit the formation of tar. Therefore, the yield of activated carbon produced by using $ZnCl_2$ and H_3PO_4 was higher than the activated carbon without activating agent. During the mixing process, $ZnCl_2$ and H_3PO_4 are involved in the degradation of cellulosic material, and further carbonization generated dehydration which results in charring and aromatization of the carbon skeleton. Thus, a porous structure was developed at the end of the process [17,29].

3.2. Elemental Analysis of Produced Activated Carbons

A low ash content with the high volatile matter of any feedstock makes it a potential source for activated carbon production. Interestingly, in our case, as presented in Table 1, both the coffee waste and empty fruit bunch feedstocks contain high volatile matter (83.6% and 74.2%) and low ash contents (1.3% and 5.4%), respectively, making them acceptable enough for their carbonization. For such feedstocks, as already reported in previous articles, an increase in the carbonizing temperature may decrease the amount of volatile matter due to further cracking of these fractions into low molecular weight liquids and gases [30,31]. In addition, the empty fruit bunch contains a higher compound of silicon 23.48 mg L^{-1}, calcium 21.71 mg L^{-1}, and iron 18.27 mg L^{-1}. On the other hand, the coffee waste contains higher magnesium, 16.66 mg L^{-1}, as reported in Table 2. So, in order to make a comparison between post carbonization elemental characteristics and their expected changes, an elemental analysis of produced activated carbons has been shown in Table 3. The percentage of carbon contents was slightly increased from 78.4 wt% to 79.8 wt% for CWAC and from 68.5 wt% to 73.3 wt% for EFBAC, respectively, by increasing the carbonization temperature from 600 °C to 800 °C. In the case of CWACK, the carbon content was at its highest at 92.7% with an activating agent mixing ratio of 1:3 and decreased slightly when the ratio decreased to 1:1 at a temperature value of 800 °C. A similar trend, with respect to activating agent mixing ratio, was also observed for 700 °C and 600 °C where the value rose from 79.4% (1:1) to 88.3% (1:3), and from 72.0% (1:1) to 78.1% (1:3), respectively. In the case of hydrogen, the lowest contents were observed with all three activating agents but at the highest temperature of 800 °C ranging from 0.2% to 1.5%. Interestingly in the case of nitrogen, the highest contents were found at the middle-value temperature (700 °C), where a gradually increasing trend was observed, with a value of 0.8% to 0.2% for KOH (1:1 to 1:3 ratios), 3.1–3.4% for $ZnCl_2$, and 2.8% for H_3PO_4 (the value kept the same). In the case of oxygen, the highest value of almost 50% was obtained with H_3PO_4 (1:3) at 800 °C. In the case of $ZnCl_2$ and KOH, these values were around 25% lower than H_3PO_4. For the values of the EFBAC, the highest carbon contents were observed at 700 °C with a $ZnCl_2$ ratio of 1:3. In this case, a similar trend was observed with either H_3PO_4 or KOH; the value exhibited a similar trend as with the coffee waste. Interestingly the nitrogen contents were rather lower than the coffee waste activated carbons, ranging only from 0.4% to 1.2%, and the oxygen contents were also in the same range as the coffee wastes, but the highest contents were found for the activating agent mixing ratio of 1:1 to 1:3 and the temperature of 700 °C with H_3PO_4.

3.3. Van Krevelen Diagram

The transformation of elemental composition with the carbonization temperature in terms of H/C and O/C ratios for biomass feedstock and activated carbons was studied by using the Van Krevelen diagram and has been demonstrated in Figure 3. It can be observed that CW resulted in a higher H/C and lower O/C compared to EFB. However, it is also clearly noticed that the H/C and O/C ratios of activated carbons generally decreased with the increase in carbonization temperature due to the loss of moisture contents in the structure of activated carbon. For CWACP and EFBACP prepared using phosphoric acid with a mixing ratio of 1:3 at 800 °C, the ratio of both the H/C and O/C increased compared

to those activated carbons prepared by using KOH and $ZnCl_2$ as activating agents. In addition, the H/C and O/C ratios of the CWACP samples were much higher compared to EFBACP. Furthermore, the activated carbons prepared by using KOH also enhanced the deoxygenation and dehydrogenation during the activation processes resulting thus in a decreased ratio of H/C and O/C.

3.4. Thermal Degradation Behavior of Activated Carbons

Thermal stability was investigated using thermal gravimetric analysis (TGA) at a constant heating rate of $10\,°C\,min^{-1}$. The thermal gravimetric analyses have been presented in terms of the volatile matters as well as fixed carbon contents of the produced activated carbons under different preparation conditions. Moreover, in Figure 4, the curves acquired from TGA data for both biomass feedstock (coffee waste and empty fruit bunch) and activated carbons have also been plotted. Here, it is quite noticeable that in the raw biomass feedstock, there are three distinct regions on the graph against the temperature line. Specifically, region 1 shows the weight loss occurred at a temperature below 100 °C, which means that moisture content was released from both biomass feedstock and activated carbons in the vapor form [32]. In addition, for regions 2 and 3, the decomposition of hemicellulose (260 °C) and cellulose (around 315–390 °C) can be considered as governing factors here as it has already been described in earlier studies [33,34]. Moreover, in Table 4, the values for the volatile matters and fixed carbon contents of both coffee waste activated carbon and empty fruit bunch activated carbon have been reported. It was found that the volatile matter of both coffee waste activated carbon and empty fruit bunch activated carbon, prepared without using an activating agent, was around 16.9 wt%, and it was gradually decreased to 11.2 wt% as the carbonization temperature was increased. For the fixed carbon content of coffee waste activated carbon, it was 83.5 wt%, 80.4 wt%, and 80.5 wt% for CWACK, CWACZ, and CWACP, respectively. Meanwhile, it was observed that the fixed carbon content decreased significantly with an increase in activating agent mixing ratio. At the same time, the fixed carbon content of empty fruit bunch activated carbon was 91.0 wt%, 89.0 wt%, and 83.1 wt% for EFBACZ, EFBACP, and EFBACK. The fixed carbon content slightly increased with an increase in activating agent mixing ratio and carbonization temperatures.

3.5. Surface Morphology of Produced Activated Carbons

The surface morphologies of the coffee waste and empty fruit bunch activated carbons were observed by field-emission scanning electron microscopy (FESEM), using an Auriga (Carl Zeiss, Germany) at various magnifications. This analysis is typical for investigating the structural pores of the activated carbons, and the corresponding images have been shown in Figures 5 and 6. The examination of surface morphology for both coffee waste activated carbon and empty fruit bunch activated carbon reveal that irregular porous surfaces have changed the pore structure during the chemical activation process as delineated in Figure 5 (the image (a)–(c) represented as CWAC carbonized at 600 °C, 700 °C, and 800 °C, respectively). The surface morphologies of CWAC exhibit somewhat smooth surfaces, including many irregular small cavities over the surface. Thus, it does not show any significant nitrogen adsorption, which could be an indication of the absence of a porous structure and low specific surface area, as reported in Table 5. Meanwhile, the CWACK sample prepared with an activating agent mixing ratio of (1:3) with different carbonization temperatures as presented in Figure 5d–f, shows that the surface morphologies contained a large number of different holes or pores shaped like a honeycomb. It could be explained that the new pores are formed due to the reaction between the carbon and activating agent during the chemical activation process [35]. Meanwhile, this also corresponds to the results of its high specific surface area and increment in total pore volume as well as micropore volume, which has been reported in Table 5. However, at the same time, CWACZ and CWACP samples which were prepared with an activating agent mixing ratio of (1:3) shown in Figure 5g–l, exhibit the developed pore shapes on the

activated carbon mainly depending on the activating agent mixing ratio and carbonization temperatures. Moreover, the external surface of the activated carbon has generated pores of various sizes and shapes. The surface morphologies of empty fruit bunch activated carbon prepared under various activating agents, mixing ratios and different carbonization temperatures are shown in Figure 6. In this Figure, images (a)–(c) represent EFBAC carbonized at 600 °C, 700 °C, and 800 °C. It is quite noticeable here that the carbonization temperature propagated slight cracks on activated carbons' surfaces which ultimately led to the generation of pores. Whereas Figure 6d–f images indicated as EFBACK show that many large pores are well developed on the surface of the activated carbon. Simultaneously, Figure 6 g–i and j–l represents EFBACZ and EFBACP, respectively, which have also generated different pore sizes as well as pore shapes upon their surface. According to previous studies [17,32] the pore generation process, in principle, occurs due to the evaporation of activating agent throughout carbonization, subsequently leaving a space in the structure of the activated carbon.

Table 5. BET surface area of coffee waste activated carbon prepared at various conditions.

Sample	Temperature (°C)	Ratio (w/w)	S_{BET} [a] (m^2/g)	V_{total} [b] (cm^3/g)	V_{micro} [c] (cm^3/g)	V_{meso} [d] (cm^3/g)	D_{avg} [e] (nm)
CWAC	600	1:0	0.00	0.00	0.00	0.00	1.33
	700	1:0	0.40	0.00	0.00	0.00	1.98
	800	1:0	1.07	0.00	0.00	0.00	10.98
CWACK	600	1:1	1162	0.47	0.45	0.04	1.62
	700	1:1	1642	0.67	0.63	0.06	1.63
	800	1:1	1912	0.82	0.77	0.12	1.72
CWACZ	600	1:1	1060	0.66	0.44	0.32	2.49
	700	1:1	990	0.61	0.41	0.29	2.47
	800	1:1	851	0.53	0.35	0.26	2.50
CWACP	600	1:1	554	0.34	0.24	0.16	2.44
	700	1:1	320	0.22	0.13	0.12	2.70
	800	1:1	381	0.23	0.13	0.10	2.37
CWACK	600	1:3	2218	1.19	1.04	0.52	2.15
	700	1:3	2934	1.94	1.64	1.31	2.65
	800	1:3	3068	2.86	1.33	2.46	3.73
CWACZ	600	1:3	1074	1.55	0.25	1.31	5.77
	700	1:3	986	1.32	0.24	1.10	5.36
	800	1:3	939	1.23	0.24	1.00	5.22
CWACP	600	1:3	524	0.52	0.17	0.38	3.97
	700	1:3	346	0.37	0.11	0.29	4.32
	800	1:3	372	0.35	0.13	0.24	3.74

[a] BET specific surface area measured by N_2 adsorption data in the P/P_0 range from 0.06 to 0.20. [b] Total pore volume determined from the adsorption isotherm at $P/P_0 = 0.99$. [c] Micropore volume calculated using a t-plot method. [d] Mesopore volume calculated by using a BJH method. [e] Average pore diameter determined by the adsorption data using a BET-plot method.

3.6. Determination of Surface Area and Pore Volume of Activated Carbons

A Brunauer–Emmett–Teller (BET) analysis for specific surface area and pore volume are given in Tables 5 and 6 for coffee waste activated carbon and empty fruit bunch activated carbon, respectively. The specific surface areas of CWAC and EFBAC were very low with a value of 1.07 m^2/g and 71.59 m^2/g, respectively, at 800 °C and 700 °C. For coffee waste activated carbon produced with KOH (CWACK), it could also be observed that as the mixing ratio of KOH increased to 1:3, the specific surface area and total pore volume were dramatically increased from 2218 m^2/g to 3068 m^2/g and 1.19 cm^3/g to 2.86 cm^3/g at a carbonization temperature of 600 °C and 800 °C. These results are even greater than previous studies [36]. Meanwhile, the specific surface area and total pore volume of coffee waste activated carbon prepared with $ZnCl_2$ (CWACZ) and H_3PO_4 (CWACP) with a mixing ratio of 1:3 were significantly decreased by increasing carbonization temperatures. For specific surface area, these values were decreased from 1074 m^2/g to 986 m^2/g and

939 m^2/g with a corresponding total pore volume of 1.55 cm^3/g to 1.32 cm^3/g, and 1.23 cm^3/g for CWACZ. CWACP decreased from 524 m^2/g to 346 m^2/g and 372 m^2/g with a corresponding total pore volume of 0.52 cm^3/g to 0.37 cm^3/g and 0.35 cm^3/g at 600 °C, 700 °C, and 800 °C, respectively.

Table 6. BET surface area of empty fruit bunch activated carbon prepared at various conditions.

Sample	Temperature (°C)	Ratio (*w/w*)	S_{BET} [a] (m^2/g)	V_{total} [b] (cm^3/g)	V_{micro} [c] (cm^3/g)	V_{meso} [d] (cm^3/g)	D_{avg} [e] (nm)
EFBAC	600	1:0	59.69	0.04	0.00	0.00	2.72
	700	1:0	71.59	0.02	0.00	0.00	1.37
	800	1:0	38.37	0.01	0.00	0.00	1.20
EFBACK	600	1:1	720	0.34	0.29	0.05	1.88
	700	1:1	948	0.43	0.36	0.07	1.80
	800	1:1	1214	0.63	0.48	0.19	2.08
EFBACZ	600	1:1	1083	0.66	0.55	0.32	2.42
	700	1:1	947	0.57	0.44	0.28	2.41
	800	1:1	945	0.55	0.45	0.25	2.32
EFBACP	600	1:1	651	0.48	0.31	0.30	2.94
	700	1:1	531	0.40	0.24	0.25	3.01
	800	1:1	646	0.44	0.31	0.24	2.70
EFBACK	600	1:3	1229	0.57	0.52	0.12	1.85
	700	1:3	1610	0.80	0.75	0.23	1.99
	800	1:3	2147	1.31	1.17	0.70	2.44
EFBACZ	600	1:3	1278	1.27	0.60	0.99	3.98
	700	1:3	1261	1.07	0.65	0.75	3.40
	800	1:3	1219	1.05	0.57	0.76	3.45
EFBACP	600	1:3	932	1.20	0.11	1.05	5.14
	700	1:3	626	0.63	0.20	0.50	4.02
	800	1:3	753	0.63	0.27	0.45	3.35

[a] BET specific surface area measured by N_2 adsorption data in the P/P_0 range from 0.06 to 0.20. [b] Total pore volume determined from the adsorption isotherm at $P/P_0 = 0.99$. [c] Micropore volume calculated using a t-plot method. [d] Mesopore volume calculated by using a BJH method. [e] Average pore diameter determined by the adsorption data using a BET-plot method.

Actually, increasing the carbonization temperature to a higher value of 800 °C led to a decrease in the specific surface area and pore volume. This reduction in area and pore volume can be anticipated due to the sintering effects at high temperatures that triggered the shrinkage of the char and realignment of the carbon structure [37,38]. In addition, the mixing ratio of the activating agent together with this carbonization temperature also played a role in significantly affecting the specific surface area and pore volume of the activated carbon. Hence it can be conclusively suggested that the activated carbon prepared with H_3PO_4 at a carbonization temperature below 600 °C will exhibit higher BET surface properties [39–42].

Interestingly, our results also prove that both mixing ratio and carbonization temperature strongly affect the properties of activated carbon. Therefore, a suitable mixing ratio and carbonization temperature should be selected for the production of activated carbon with a high specific surface area and pore volume. The specific surface area and total pore volume of empty fruit bunch activated carbon prepared with KOH (EFBACK) with an activating agent mixing ratio of (1:3) resulted in the highest value, starting from 1229 m^2/g, 1610 m^2/g, and 2147 m^2/g, to 0.57 cm^3/g, 0.80 cm^3/g, and 1.31 cm^3/g with activation at 600 °C, 700 °C, and 800 °C. At the same time, empty fruit bunch activated carbon produced with $ZnCl_2$ (EFBACZ), and H_3PO_4 (EFBACP) exhibited a rather low specific surface area from 1278 m^2/g, 1261 m^2/g, and 1219 m^2/g, to 932 m^2/g, 626 m^2/g, and 753 m^2/g. Nevertheless, they also exhibited a low total pore volume starting from 1.27 cm^3/g, 1.07 cm^3/g, and 1.05 cm^3/g, to 1.20 cm^3/g, 0.63 cm^3/g, and 0.63 cm^3/g at 600 °C, 700 °C, and 800 °C, respectively. Our finding is also in comparison with the previous studies. For example, in one previous study [43], it was reported that chemical activation by using $ZnCl_2$ and

H_3PO_4 at a carbonization temperature of 500 °C yielded the best results. Interestingly in our case, the specific surface area together with the micropore volume exhibited a reverse behavior with an increase in the corresponding carbonization temperatures.

Nonetheless, from our findings, it can be conclusively suggested that such kind of activated carbon products are capable enough to be applied in the wastewater treatment processes. For such processes, activated carbons, due to the large surface area, give exceptional adsorption qualities destined to purify the contaminated water not only by discoloring but also by removing the odors with enhanced efficiency in an economical way [20,32,44].

4. Conclusions

Coffee waste and empty fruit bunches were successfully carbonized for the preparation and characterization of activated carbons. According to the results, it could be observed that the activating agent mixing ratio and the carbonization temperature showed a great influence on the yields of produced activated carbons. At the same time, it was clearly seen that the high specific surface area and total pore volume were found maximum at 800 °C in either case of the substrate. Meanwhile, the specific surface area and total pore volume of the activated carbon prepared by using $ZnCl_2$ and H_3PO_4 were significantly decreased by increasing the activating agent mixing ratio and carbonization temperatures. The experimental results showed that agricultural byproducts and organic wastes could be utilized as a precursor for activated carbon production in an economical yet environmentally friendly way.

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