

The Physical and Chemical Properties of Activated Nanocarbon Produced from Robusta (*Coffea Canephora*) Coffee Pulp under slow pyrolysis method

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ABSTRACT

This study examines the physical and chemical properties of nano-activated carbon obtained from Robusta coffee pulp. It also examines the potential use of Robusta coffee pulp biomass as a raw material for hydrogen storage. In this investigation, the dried coffee pulp samples were carbonized using the slow pyrolysis method at temperatures of 400°C and 500°C. A biochar product was obtained and activated using NaOH and ZnCl₂ solutions. The analysis results Fourier Transform Infra-Red (FTIR) suggested that both carbonization and activation processes with NaOH or ZnCl₂ solutions were unable to removed the caffeine content in coffee pulp. The Differential Calorimetric Analysis/Thermogravimetric Analysis (DSC/TGA) indicated that coffee pulp carbonization reached optimality within the temperature range of 400 to 500°C. Furthermore, the Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM/EDS) and N₂-adsorption isothermal analysis showed that the surface pores of activated carbon had a honeycomb-like structure with a size greater than 0.7 nm which is applicable for hydrogen storage material.

Key words: Activated carbon; Robusta coffee pulp; Slow pyrolysis; Surface area.

1 INTRODUCTION

Activated carbon is a porous material that can be used as an adsorbent medium for certain liquids and gases. It is popularly used in air and water purification technology. Commercial activated carbon is obtained from methane or phenol which is a derivative product of fossil fuels. However, its manufacturing process is expensive and has the potential to pollute the environment (Xia; Yang; Zhu, 2015). There was an increased study on the depletion of raw materials used for the manufacture of activated carbon from fossil fuel derivative products such as petroleum and coal. This was carried out to obtain activated carbon from biomass raw materials. Furthermore, considering the increasing activated carbon need, the world's consumption in 2014 alone reached 1.7 million tons per year (Esterlita; Herlina, 2015). Therefore, developing alternative ways of producing activated carbon was an inevitable trend.

Indonesia is the fourth largest coffee-producing country in the world after Brazil, Vietnam, and Columbia (Amarocho-Cruz; Cortés, 2021). However, this country still imports activated carbon even though the raw material can be easily obtained domestically. The carbon can be treated from agriculture, plantation biomass, and industrial wastes such as coal fly ash waste. One of the potential sources for producing activated carbon is coffee plant waste. The biggest waste from this plant is the skin of the coffee bean. Furthermore, the average

coffee skin production reaches 2.2 tons.ha⁻¹ per year, where 1 kg of freshly picked coffee contains almost 50% by weight of wet skin (Janissen; Huynh, 2018). This wet-processed coffee skin is known as coffee pulp. In the Gayo Highlands, Aceh Province, people generally use coffee skin waste as a mixture of animal feed and additional fertilizer for vegetable crops. Meanwhile, in some cases it was not used and had the potential to pollute the surrounding environment. The content of phenolic compounds, tannins, caffeine, and chlorogenic acid (Janissen; Huynh, 2018) limits usage in animal feed due to its anti-nutritive properties. Developmental, behavioral and morphological abnormalities were observed in various aquatic organisms (Rodriguez et al., 2014) and tannins (Meriç et al., 2005) including algae, sea urchins, and fishes due to caffeine exposure. Similarly, the presence of chlorogenic acid limited the application of coffee skin as a plant fertilizer due to its phytotoxic nature to the formation of plant roots. There is ample evidence that these bioactive compounds are a concern to ecotoxicologists. This is due to the harmful substances from coffee products which may harm the ecosystem by reaching the soil surface and watercourses (Franklin; Dias, 2011). Therefore, technology is needed to utilize coffee skin waste into something more useful, one of which is activated carbon material that can be used as an adsorbent for gas or liquid. This material was known to have a high hydrogen storage capacity due to its porous microstructure and high specific surface area which is even higher than the

hydrogen storage capacity of graphite and carbon nanotube materials (Lototsky et al., 2015).

Pyrolysis is a simple technology that converts coffee pulp waste into carbon. It is the method of processing biomass into carbon, tar, and syngas at high temperatures. The carbon from pyrolysis is activated physically using high temperatures and chemically using chemical solutions such as NaOH, ZnCl₂, KOH, e.t.c (Angin, 2014). Furthermore, it was reported that micro-porous activated carbon was manufactured from coffee bean waste through KOH activation. The ability to store hydrogen at a temperature of 298 K increased linearly and was in direct proportion with the specific surface area observed at temperatures of 298 K and 77 K. The maximum amount of hydrogen absorption was 0.6 wt.% on carbon with a specific surface area of 2070 m²/g. Meanwhile, at a temperature of 77 K the absorption was 4.0% by weight for the same sample. The specific surface area of activated carbon plays an important role and correlates with an increase in the ability of activated carbon to absorb gases and liquids. The increased porosity of activated carbon also potentially reduces mass density and increases gas absorption capacity (Akasaka et al., 2011a).

Activated carbon from the coffee endocarp was also investigated based on the preparation conditions, activation temperature of 1073 K, activation time of 10 minutes, and mass ratio 3:1 of KOH and carbon. The Brunauer Emmette Teller (BET)

specific surface area value, total pore volume, and water vapor adsorption capacity of an optimally activated carbon endocarp coffee were 2349, m²/g, 1.036 cm³/g, and 0.7409 g/g, respectively (Sun et al., 2019). Table 1 shows the pore characteristics of activated carbon from various types of biomass materials.

Several studies showed that activated carbon derived from biomass is potentially an adsorbent for dehumidification in solar energy drying systems. This indicates coffee plant waste can be used as a source of activated carbon raw material. Furthermore, the carbonization process of Gayo Robusta coffee (*Coffea canephora*) from plantations in the Bener Meriah Regency was carried out through the slow pyrolysis method. This process showed a promising potential for the utilization of coffee waste as a raw material in the manufacture of activated carbon used as adsorbents (Raihan; Setiawan; Hakim, 2020). However, it is still necessary to further examine the effect of pyrolysis temperature and activating agent on the physical and chemical properties of activated carbon derived from Robusta Gayo coffee pulp. Therefore, this study aims to determine the effect of pyrolysis temperature and activating solution on the characteristics of coffee pulp-activated carbon samples. This is based on the FTIR test for identification of functional groups and chemical groups, DSC/TGA test for identification of thermal properties, micropore analysis by BET spectroscopy, and morphological analysis obtained by SEM/EDS test.

Table 1: Data of activated carbon from different studies.

Feedstock	Surface area, BET (m ² /g)	Micropore volume (cm ³ /g)	Pore diameter (nm)	Ref.
Walnut shells	420.5			(Hajjaligol; Masoum, 2019)
Empty fruit bunch	687	0.297	1.954 - 2.109	(Arshad et al., 2016)
	3012	0.98		(Sun; Webley, 2010)
Corn cob	3530	1.94		(Zhang et al., 2013)
	1600		(Rajalakshmi et al., 2015)	
Hemp stem	3241	1,98		(Yang et al., 2012)
Coconut shell	2800	1.39		(Jin; Lee; Hong, 2007)
Litchi wood	2623	0.72		(Huang et al., 2010)
Anthracites	3220	1.02		(Fierro et al., 2010)
Jute	1224	0.43		(Ramesh et al., 2017)
Rice hull				(Chen et al., 2012)
Coffee bean	2070			(Akasaka et al., 2011b)
Phyllostachys bambusoides	679.8			(Jang et al., 2019)
Bamboo Charcoal	3208	1.01		(Zhao et al., 2017)
Coconut Meat				(Dixit et al., 2014)
Pinecone	1173	0.4513		(Stelitano et al., 2020)
Rice fibers	2260			(Hwang et al., 2016)
Paper mulberry	1331			(Hwang et al., 2016)
Tamarind seeds	1785	0.94		(Ramesh et al., 2015)
Melaleuca bark	3170			(Xiao et al., 2014)

2 MATERIAL AND METHOD

2.1 Material

The material used was the Gayo Robusta coffee skin, supplied from Bener Meriah Regency, Gayo Highlands, Aceh Province, Indonesia. The activator solution was 2% and 10% of NaOH (Merck) and ZnCl₂ (Merck), respectively. Also, the equipment used consisted of a pyrolysis reactor, oven, scales, 50 mesh sieve, and glass beaker.

2.2 Coffee Pulp Preparation and Carbonization

The coffee pulp (CP) was collected from one of coffee plantations at Bener Meriah Regency. It was cleaned of dirt and dried under the sun until it reached a moisture content of 5% to 10%. Afterward, the CP weighed three kg and was placed in the pyrolysis reactor for the carbonization process (Raihan; Setiawan; Hakim, 2020). CP Heating was carried out in the reactor at 400 °C and 500 °C for 3 hours and cooled to room temperature. The pyrolysis product in biochar (carbon) form was then collected and mashed using a mortar and pestle until a uniform grain size that passed through a 50 mesh sieve was obtained. The carbon samples were denoted C400 and C500, respectively.

2.3 Activated carbon

Samples C400 and C500 were activated by chemical solution impregnation. A total of 10 grams of each sample was immersed in 100 mL of chemical solution for 24 hours at room temperature. The samples were filtered and washed using filter paper and distilled water, respectively, until the washing effluent reached a neutral pH. Furthermore, all samples were dried in an oven at 105 °C for 30 minutes before being analyzed and characterized. The carbon samples activated with 2% NaOH solution were named AC400a2 and AC500a2. Meanwhile, the carbon samples activated with 10% ZnCl₂ solution were named AC400b10 and AC500b10. The manufacturing scheme and process parameters of all samples are shown in Figure 1 and Table 2, respectively.

2.4 Characterization

2.4.1 FTIR Analysis

The surface functional groups of all samples was determined by Fourier-transform Infrared Spectroscopy (FTIR) using a SHIMADZU IR Prestige 21 apparatus. This was carried out between a wavelength of 400-4000 cm⁻¹, with a resolution of 41 cm⁻¹ and 45 scanners. FTIR was able to accurately detect differences between compounds in coffee varieties (Amorocho-Cruz; Cortés, 2021).

2.4.2 SEM-EDS Analysis

The surface topography, chemical composition and pore structure of the samples were analyzed using Scanning Electron Microscope with the JEOL-JSM-6510LV EDS detector.

2.4.3 N₂-physisorption Analysis

To determine the surface area and pore structure of activated carbon samples, a nitrogen adsorption-desorption isotherm test was carried out at 77.3K using an automatic adsorption apparatus, Nova Quantachrome Instruments version 11.03 (Quantachrome Corporation, USA). Adsorption data were obtained at a relative pressure, P/P₀, ranging from 0.01 to 0.1. Before testing, the sample was degassed inside a vacuum for 3 hours at a temperature of 300 °C. Data calculation and analysis was carried out following BET method.

2.4.4 DSC-TGA Analysis

The thermal dehydration properties of the samples under nitrogen atmosphere were tested using a Mettler Toledo TGA/DSC apparatus at a flow and heating rate of 30 ml/min and 15 C/min, respectively. Furthermore, the sample was placed in an alumina container weighing 10 mg and heated from room temperature to 600 °C. The TGA curve showed a change in heated sample mass as a function of temperature. Meanwhile, the DSC curve showed a quantitative measurement of the enthalpy change which occurred in a sample as a function of temperature during heating.

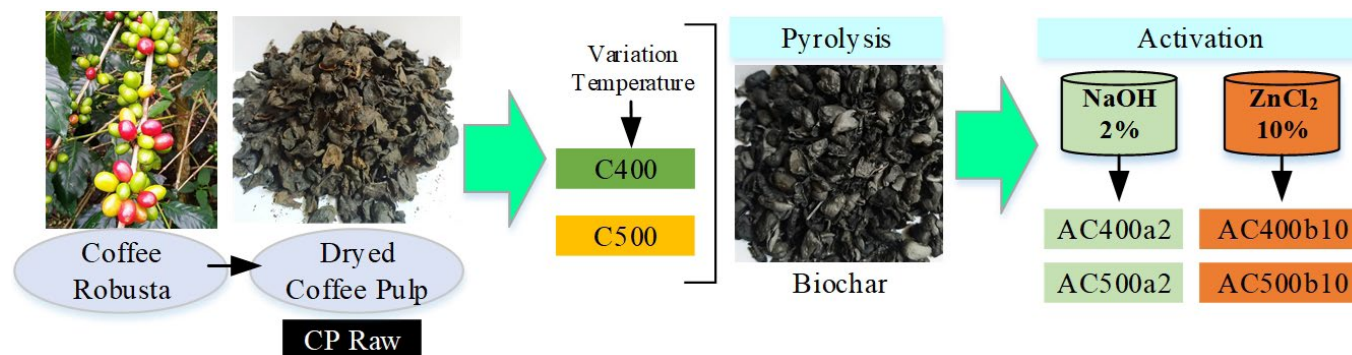


Figure 1: Activated Carbon Preparation Process Diagram.

Table 2: Parameters of samples.

No	Sample code	Temperature of pyrolysis	Chemical activator	
1	CP	-	-	Raw Material
2	C400	400 °C	-	Biochar (Carbon)
3	C500	500 °C	-	Biochar (Carbon)
4	AC400a2	400 °C	NaOH 2%	Activated Carbon
5	AC500a2	500 °C		
6	AC400b10	400 °C	ZnCl ₂ 10%	Activated Carbon
7	AC500b10	500 °C		

3 RESULTS

3.1 FTIR spectra

The FTIR analysis was used to determine the number of functional groups related to the presence of certain compounds in coffee pulp such as carbohydrates, fats, chlorogenic acid, caffeine, protein, and water (Amorocho-Cruz; Cortés, 2021). In Figure 2, the FTIR spectrum of coffee pulps derived from Gayo robusta coffee (CP sample) was shown. This was activated using carbon (AC400a2, AC400b10, AC500a2, and AC500b10 samples) and modified through pyrolysis techniques at 400C and 500C (C400 and C500 samples).

For raw CP samples, vibrations at 3275 cm⁻¹ were associated with the H₂O molecular band (Amorocho-Cruz; Cortés, 2021), while those around 2941-2829 cm⁻¹ were associated with the presence of methylxanthine as caffeine

(Craig; Franca; Oliveira, 2012). A wavelength of 3000-2700 cm⁻¹ coincides with molecular vibrations (Amorocho-Cruz; Cortés, 2021) and (Craig; Franca; Oliveira, 2012). Furthermore, vibrations of about 2142 cm⁻¹ were associated with the presence of protein (Belchior et al., 2020), while those within wavelengths of 1700-1600 cm⁻¹ were associated with molecular vibrations of caffeine molecules (Craig; Franca; Oliveira, 2011). The presence of the amino acid tyrosine was indicated by vibrations at a wavelength of 1543 cm⁻¹ (Garcia-Freites; Röder; Thornley, 2020). Chlorogenic acid was also indicated by a band area range of 1404-1242 cm⁻¹, while vibrations at 1029 cm⁻¹ were associated with carbohydrate molecules (Amorocho-Cruz; Cortés, 2021). Caffeine and chlorogenic acids were the dominant compounds in Robusta Gayo Coffee pulp. All the modified coffee pulp samples showed changes in most of the compound content. Furthermore, the heating process damaged carbohydrates, proteins, and most of the chlorogenic acids. However, caffeine compounds of wavelength vibration within 2941-2829 cm⁻¹ could not be removed by heating at a temperature of 500C or activated by a solution of NaOH and ZnCl₂. This study showed that caffeine is a very strong compound contained in coffee pulp and cannot be removed even after heating to a high enough temperature. This heating leads to the conversion of coffee pulp into carbon (biochar) followed by modification using chemical solutions to convert it into activated carbon.

3.2 SEM Images and EDS Spectra

Figure 3(a-e) shows an SEM/EDS image of activated carbon from Robusta Gayo coffee pulp. The CP Raw

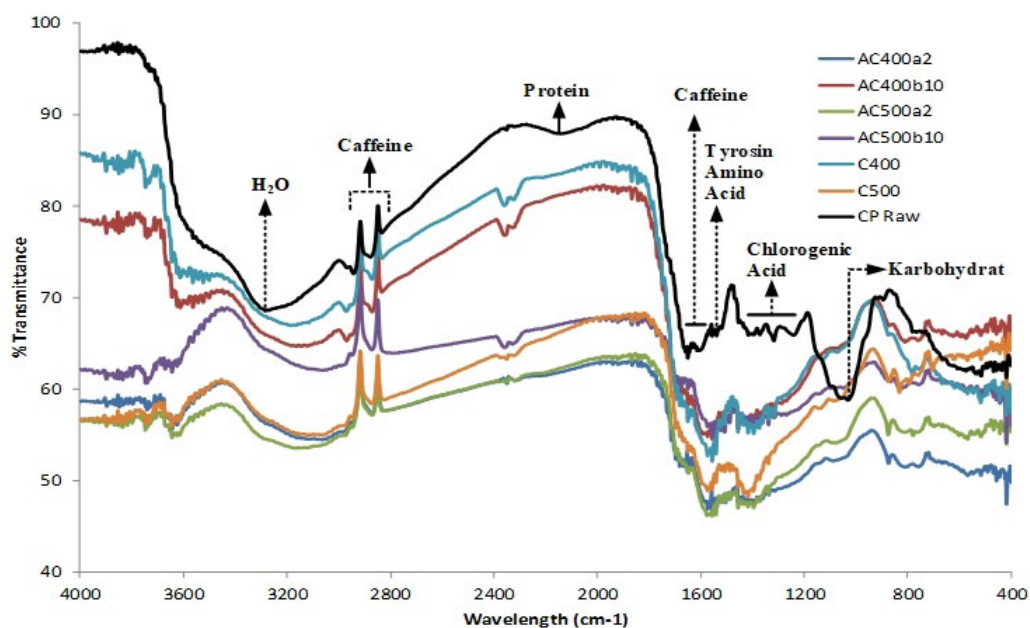


Figure 2: FTIR spectra of raw material, biochar and activated carbon samples.

sample (Figure 3a) shows a smooth surface structure with fractures and piles of irregular and layered grains. All the modified coffee pulp samples in Figure 3 (b-e) had several pores on the surface. Some of these pores were covered with hydrocarbons which shows the pore structure with excellent mechanical properties in a honeycomb-like structural arrangement (Arshad et al., 2016). Furthermore, the porous structure on the surface caused carbon and activated carbon materials to obtain adsorbent ability in certain liquids or gases by physisorption. This indicates these materials can be used as gas storage materials and as adsorbents for water and air purification (Hwang et al., 2016). The EDS spectrum of all modified coffee pulp samples showed an increase in the content of carbon atoms (C) and a decrease in the content of other atoms (O, K, S, Si, Mg, Ca, Al, and P). This proves that the process of modifying coffee pulp into activated carbon was successfully carried out.

The decrease in O, K, S, Ca, and Mg atoms and the disappearance of P, Si, and Al atoms shown in the EDS spectrum of modified coffee pulp sample corresponded to the FTIR spectrum. The process of pyrolysis and activation using chemical solutions changed most of the compound content and removed certain compounds in the coffee pulp samples, except for caffeine which was still present in all samples. This was indicated by infrared absorption in the wave band around 2941-2829 cm^{-1} . The appearance of Na and Cl atoms in the EDS spectrum of all activated carbon samples indicates that the sample stages washing process after activation using NaOH or ZnCl₂ solution were less effective. However, there were impurities from the chemical activator residue in the activated carbon sample. From Figure 3(e) it is quite clear that some of the impurities filled the pores on the surface of the activated carbon sample.

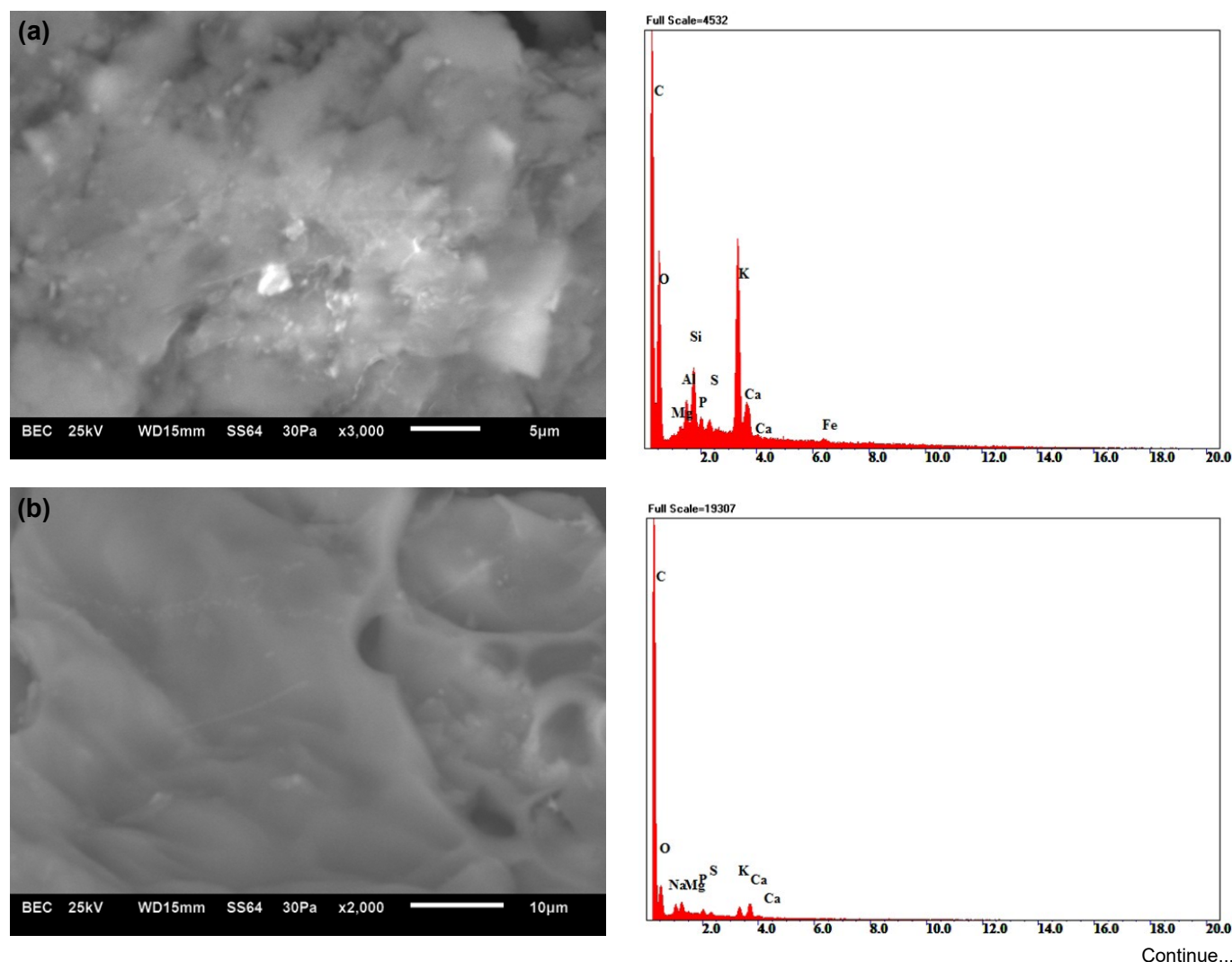


Figure 3: SEM Images and EDS spectra of (a) CP Raw, (b) AC400a2, (c) AC500a2, (d) AC400b10, (e) AC500b10.

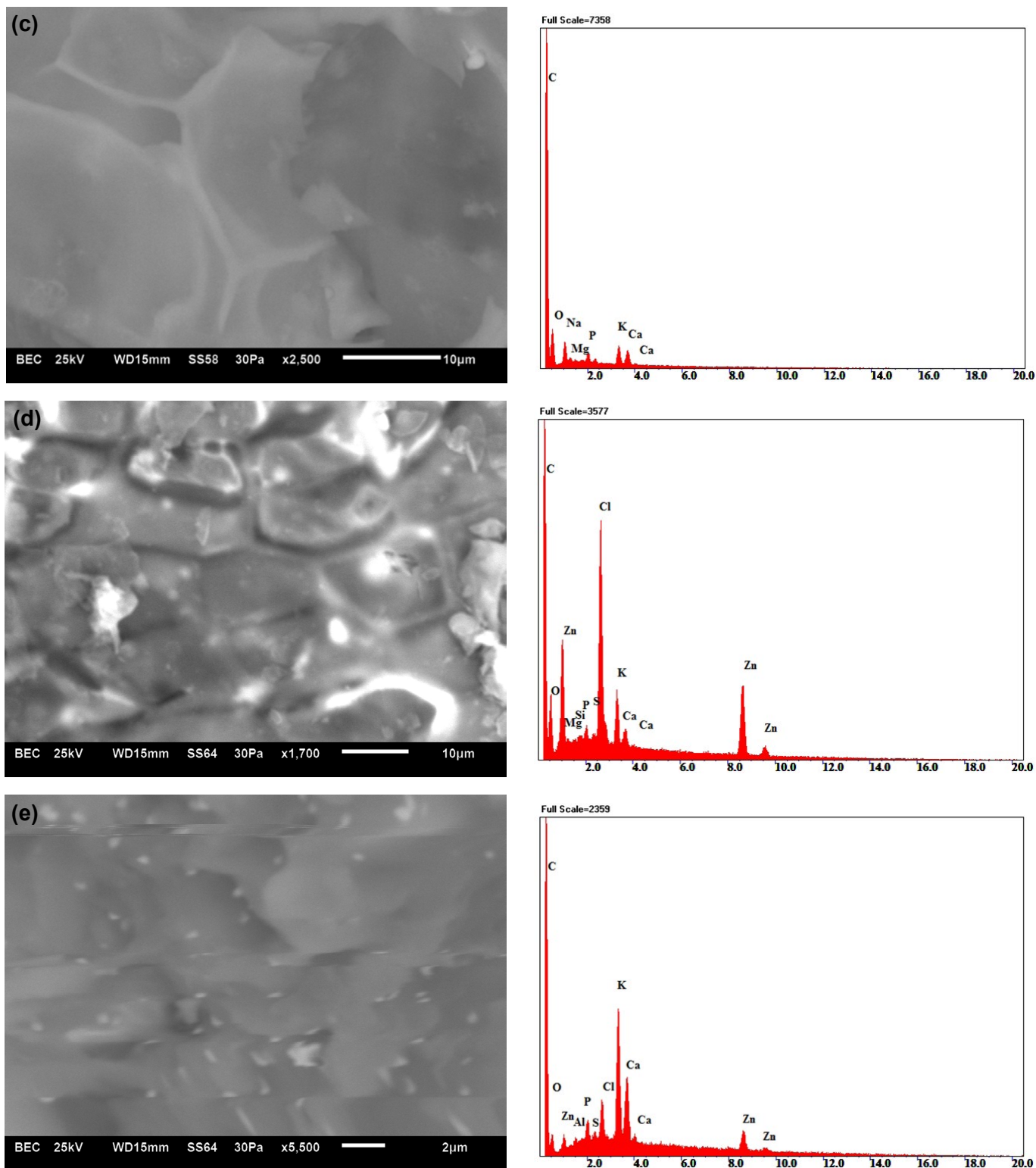


Figure 3: Continuation...

3.3 BET Analysis Results

Table 3 shows the pore characteristics on the surface of the modified coffee pulp Robusta Gayo sample. Although in this study, the nitrogen absorption test at low pressure was more supportive of the desorption value. The highest surface

area value was shown by the coffee pulp sample pyrolyzed at a temperature of 400 °C. An increase in this pyrolysis temperature to 500 °C reduces the surface area of the sample and the formation of carbon with surface pores due to high temperatures which burn raw materials (Raihan; Setiawan; Hakim, 2020).

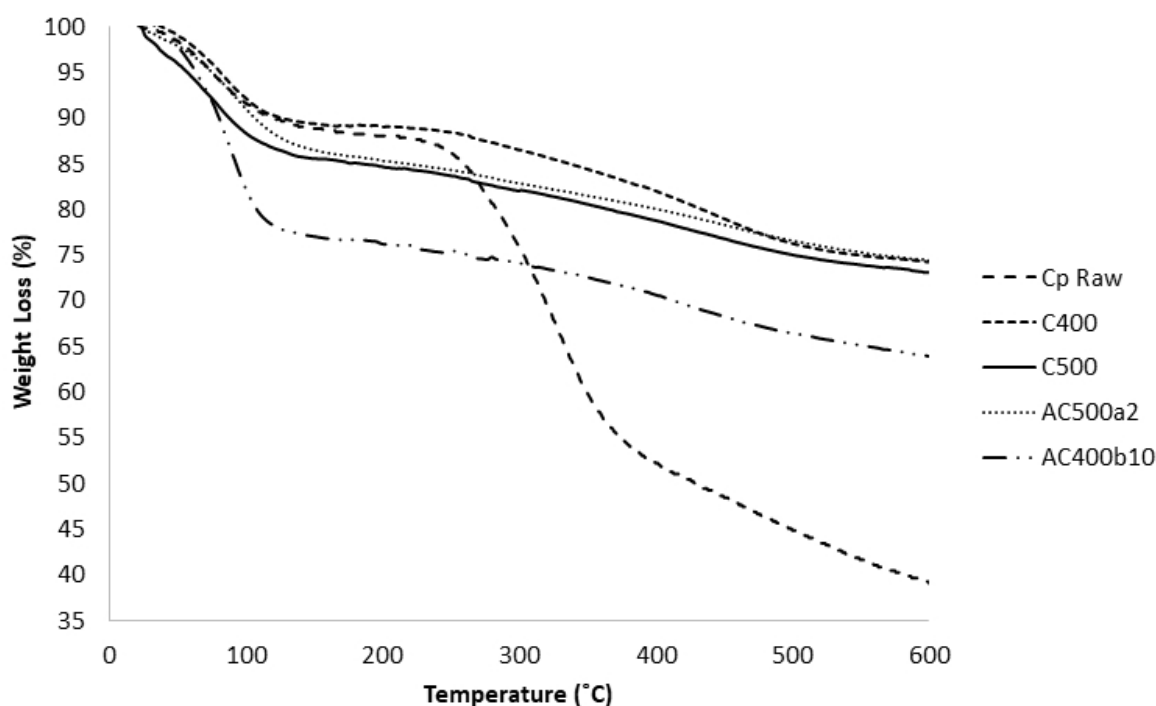
Table 3: Pore Characteristics.

No	Sample code	Surface area (m ² /g)	Pore Volume (cc/g)	Pore diameter (Å)
1	C400	187.3	0.025	9.24
2	C500	176.4	0.024	8.46
3	AC400b	164.1	0.022	9.36
4	AC500a	158.3	0.022	9.16

Furthermore, the nitrogen uptake test also showed that the pore quality on the carbon sample surface which was activated by a chemical solution decreased. This is following the results of the sample's SEM images which show the presence of impurities in the form of chemical solution residues. These residues were still present in sample surface pores after the washing process during the activation stage to form activated carbon. All the samples of carbon and activated carbon produced in this study are potentially hydrogen storage materials due to a pore size greater than 0.7 nm (Zhao et al., 2011). Hydrogen has been widely recognized as a future ideal energy source due to its abundant availability in nature. Also, carbon-based materials were considered useful for hydrogen storage and have several advantages being lightweight and having a large specific surface area (Zhao et al., 2017).

3.4 DSC-TGA Curves

Figures 4 and 5 show the plot of the DSC/TGA spectrum for modified and untreated coffee pulp samples.

**Figure 4:** TGA curves of CP Raw, CP400, CP500, AC500a2, and AC400b10 samples.

The thermal decomposition process of coffee pulp while heating in a nitrogen atmosphere was observed from room temperature to 600 °C in inert nitrogen gas. Furthermore, the TGA graph shows that its mass decomposition (Figure 4) occurs in three stages. Mass loss in the first stage is caused by water molecule dehydration which fills the pores of the sample and some volatile substances including some carbohydrates. This stage occurs from room temperature to a temperature of about 155 °C with a mass loss of up to 15%. In the DSC graph (Figure 5), it shows an endothermic reaction stage where the peak of the reaction is at a temperature of around 80 °C involving heat energy of about 1.68 Joules. Furthermore, the second stage of the coffee pulp mass loss process occurs within a temperature range of 252 °C - 395 °C with a mass reduction of nearly 40%. There is a massive devolatilization process of the coffee pulp constituent materials such as carbohydrates, lipids, some proteins, and lignin (Setiawan et al., 2020). The third stage occurred until a temperature of 600 °C was reached where little material was lost through burning. Therefore, based on the TGA graph, it can be concluded that temperatures within 400-500 °C are quite effective for coffee pulp carbonization process. This is reinforced by the TGA graph of sample C400 which shows that reheating of carbon samples from the carbonization process of coffee pulp does not lead to a significant mass loss of 500 °C. Furthermore, at a temperature range above 500 °C, the gas evolution phase occurs, where solid carbon reacts with water vapor or carbon dioxide which is converted into carbon monoxide and hydrogen (Nikoo; Amin, 2011).

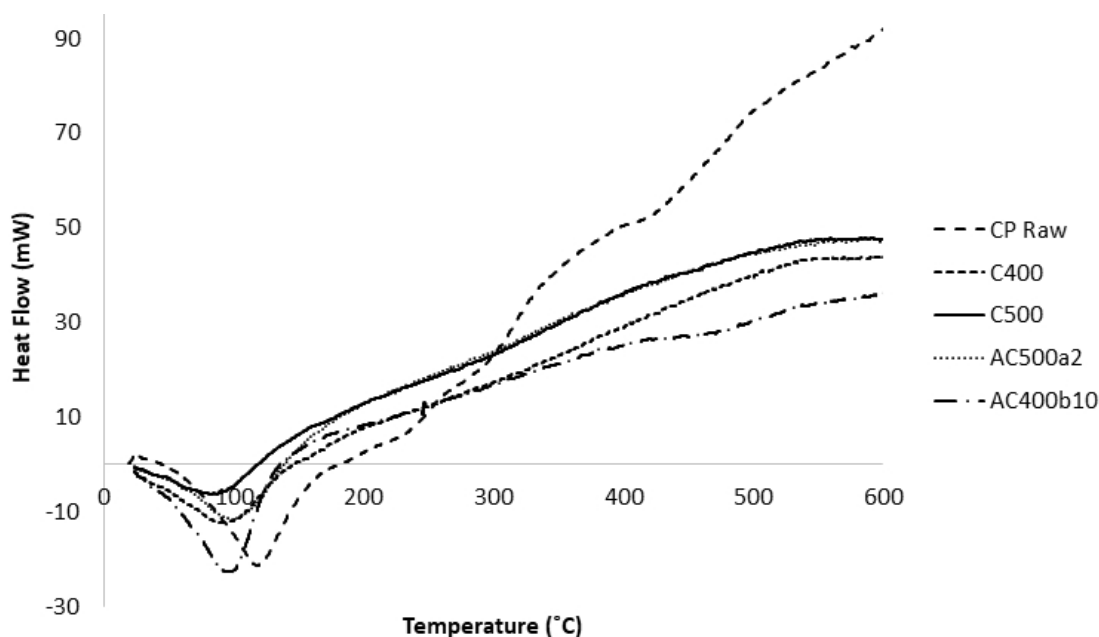


Figure 5: DSC curves of CP Raw, AC400, AC500, AC500a2 and AC400b10 samples.

4 DISCUSSION

The pyrolysis process for temperatures of 400 °C and 500 °C on Robusta Gayo coffee pulp produced biochar, tar, and non-condensable gas. More biochar content was obtained at a pyrolysis temperature of 400 °C compared to 500 °C. From a thermal decomposition test, the pulp carbonization was quite effective at temperatures of 400-500 °C. The FTIR spectrum also showed that coffee pulp contained caffeine, carbohydrates/protein, lipid, and chlorogenic acid (Amorocho-Cruz; Cortés, 2021), where caffeine and chlorogenic acid were dominant. These compounds can be used as anti-obesity, anti-inflammatory, and other effects. FTIR analysis indicated that carbon and activated carbon from coffee pulp with different treatments had very similar functional groups on the surface and predominantly contained caffeine. Therefore, this study showed that neither the pyrolysis nor activation process using NaOH and ZnCl₂ solutions could eliminate the caffeine content in Robusta Gayo coffee pulp. The presence of caffeine compounds was indicated by the infrared spectrum within the band of 2877-2973 cm⁻¹ present in both modified and regular coffee pulp samples.

Morphological analysis showed that pyrolysis produces carbon with a porous surface structure where the pore structure becomes better after the carbon is activated using chemical solutions of NaOH and ZnCl₂. The EDS spectrum also showed that the pyrolysis and carbon activation increased elemental C and reduced the amount of other bound elements in the sample. A properly developed pore structure was observed in the AC500b10 sample with ZnCl₂ activation solution. This was potentially an adsorbent that stores liquids and gases. The

surface pore sample also show a honeycomb-like structure which was the most mechanically stable material structure. However, the EDS spectrum showed the presence of Zn and Cl atoms as impurities that covered some of the pores, which originated from remnants of the activator solution. This was due to the presence of impurities washing steps which were effective for reducing the surface area size.

Furthermore, the nitrogen uptake test showed that the surface area of BET carbon decreased with increasing pyrolysis temperature although it did not significantly affect the pore volume and size. The activated carbon from Robusta Gayo coffee pulp had a pore size greater than 0.7 nm, therefore, it was potentially a solid-state hydrogen storage material.

5 CONCLUSION

Based on the analysis results, it can be concluded that coffee pulp can potentially be used as an activated carbon adsorbent to store liquids and gases. The FTIR test of raw coffee pulp showed the presence of carbohydrates, chlorogenic acid, caffeine, protein, tyrosine amino acids, and water molecules related to humidity. Furthermore, modification through carbonization and chemical activation removed the content of carbohydrates, chlorogenic acid, and protein, but the content of caffeine could not be removed. This indicates the use of coffee pulp waste as a mixture of animal feed and fertilizer is not recommended. This is due to the content of caffeine compounds and chlorogenic acid which are dominant and have anti-nutritive properties in livestock land and aquatic animals that interfere with plant root growth. The thermal analysis also showed that the coffee pulp carbonization process was

completed within a temperature range of 400 °C to 500 °C. The isothermal nitrogen physisorption analysis indicated that the best pore characteristics of the activated carbon is resulted from activation using 10% ZnCl₂. All activated carbon samples obtained in this study have an average pore diameter of above 0.7 nm highlighting a potential use for hydrogen storage materials.

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7 AUTHOR CONTRIBUTIONS

NN and RR carried out the sample preparation, data collection and analysis. ZL SN and AS supervised the experiment. The first draft of the manuscript was written by NN and RR. Manuscript was finalized by NN and AS. All authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

8 REFERENCES

- AKASAKA, H. et al. Hydrogen storage ability of porous carbon material fabricated from coffee bean wastes. **International Journal of Hydrogen Energy**, 36(1):580-585, 2011a.
- AKASAKA, H. et al. Hydrogen storage ability of porous carbon material fabricated from coffee bean wastes. **International Journal of Hydrogen Energy**, 36(1):580-585, 2011b.
- AMOROCHO-CRUZ, C. M.; CORTÉS, M. Physicochemical, microbiological, and sensory characterization of fermented coffee pulp beverages. **Coffee Science**, 16:e 161889, 2021.
- ANGIN, D. Production and characterization of activated carbon from sour cherry stones by zinc chloride. **Fuel**, 115:804-811, 2014.
- BELCHIOR, V. et al. FTIR and chemometrics as effective tools in predicting the quality of specialty coffees. **Food Analytical Methods**, 13(1):275-283, 2020.
- CHEN, H. et al. High hydrogen storage capacity of rice hull based porous carbon. **International Journal of Hydrogen Energy**, 37(24):18888-18894, 2012.
- CRAIG, A. P.; FRANCA, A. S.; OLIVEIRA, L. S. Discrimination between immature and mature green coffees by attenuated total reflectance and diffuse reflectance fourier transform infrared spectroscopy. **Journal of Food Science**, 76(8): C1162-C1168, 2011.
- CRAIG, A. P.; FRANCA, A. S.; OLIVEIRA, L. S. Evaluation of the potential of FTIR and chemometrics for separation between defective and non-defective coffees. **Food Chemistry**, 132(3):1368-1374, 2012.
- DIXIT, V. et al. Hydrogen storage in carbon derived from solid endosperm of coconut. 2014. p. 1-10. Available at: <http://arxiv.org/abs/1409.7219>. Accessed on: August, 22, 2020.
- FIERRO, V. et al. Adsorption and compression contributions to hydrogen storage in activated anthracites. **International Journal of Hydrogen Energy**, 35(17):9038-9045, 2010.
- FRANKLIN, G.; DIAS, A. C. P. Chlorogenic acid participates in the regulation of shoot, root and root hair development in *Hypericum perforatum*. **Plant Physiology and Biochemistry**, 49(8):835-842, 2011.
- GARCIA-FREITES, S.; RÖDER, M.; THORNLEY, P. Environmental trade-offs associated with bioenergy from agri-residues in sub-tropical regions: A case study of the Colombian coffee sector. **Biomass and Bioenergy**, 140:105581, 2020.
- HAJIALIGOL, S.; MASOUM, S. Promising electrochemical hydrogen storage properties of nano biomass derived from walnut shell. **International Journal of Hydrogen Energy**, 44(21):10713-10721, 2019.
- HUANG, C. C. Effect of surface oxides on hydrogen storage of activated carbon. **Separation and Purification Technology**, 70:291-295, 2010.
- HWANG, S. H. et al. Hydrogen storage characteristics of carbon fibers derived from rice straw and paper mulberry. **Materials Letters**, 167:18-21, 2016.
- JANG, H. et al. Science direct the performance of green carbon as a backbone for hydrogen storage materials. **International Journal of Hydrogen Energy**, 45(17):10516-10522, 2019.
- JANISSEN, B.; HUYNH, T. Chemical composition and value-adding applications of coffee industry by-products: A review. **Resources, Conservation and Recycling**, 128:110-117, 2018.
- JIN, H.; LEE, Y. S.; HONG, I. Hydrogen adsorption characteristics of activated carbon. **Catalysis Today**, 120(3):399-406, 2007.

- LOTOTSKYY, M. V. et al. Metal hydride systems for hydrogen storage and supply for stationary and automotive low temperature PEM fuel cell power modules. **International Journal of Hydrogen Energy**, 40(35):11491-11497, 2015.
- ESTERLITA, M. O.; HERLINA, N. Pengaruh penambahan aktivator ZNCL₂, KOH, DAN H₃PO₄ dalam pembuatan karbon aktif dari pelepah aren (*Arenga Pinnata*). **Jurnal Teknik Kimia USU**, 4(1):47-52, 2015.
- ARSHAD, S. H. et al. Preparation of activated carbon from empty fruit bunch for hydrogen storage. **Journal of Energy Storage**, 8:257-261, 2016.
- MERIÇ, S. et al. Toxicity of leather tanning wastewater effluents in sea urchin early development and in marine microalgae. **Chemosphere**, 61(2):208-217, 2005.
- NIKOO, M. K.; AMIN, N. A. S. Thermodynamic analysis of carbon dioxide reforming of methane in view of solid carbon formation. **Fuel Processing Technology**, 92(3):678-691, 2011.
- RAIHAN, R.; SETIAWAN, A.; HAKIM, L. Preparation and characterization of active charcoal made from robusta coffee skin (*Coffea Canephora*). **Jurnal Rekayasa Kimia dan lingkungan**, 15(2):104-110, 2020.
- RAJALAKSHMI, N. et al. Porous carbon nanomaterial from corncob as hydrogen storage material. **Advanced Porous Materials**, 2(3):165-170, 2015.
- RAMESH, T. et al. Activated carbons derived from tamarind seeds for hydrogen storage. **Journal of Energy Storage**, 4:89-95, 2015.
- RAMESH, T. et al. Synthesis and characterization of activated carbon from jute fibers for hydrogen storage. **Renewable Energy and Environmental Sustainability**, 2(4):1-8, 2017.
- RODRIGUEZ, R. S. et al. Reversible neuronal and muscular toxicity of caffeine in developing vertebrates. **Comparative Biochemistry and Physiology Part - C: Toxicology and Pharmacology**, 163:47-54, 2014.
- SETIAWAN, A. et al. Thermal decomposition of gayo arabica coffee-pulp in a segmented chamber. **Journal of Physics: Conference Series**, 1500:012076, 2020.
- STELITANO, S. et al. Pinecone-derived activated carbons as an effective medium for hydrogen storage. **Energies**, 13(9):2237, 2020.
- SUN, S. et al. Preparation of coffee-shell activated carbon and its application for water vapor adsorption. **Renewable Energy**, 142:11-19, 2019.
- SUN, Y.; WEBLEY, P. A. Preparation of activated carbons from corncob with large specific surface area by a variety of chemical activators and their application in gas storage. **Chemical Engineering Journal**, 162(3):883-892, 2010.
- XIAO, Y. et al. Melaleuca bark based porous carbons for hydrogen storage. **International Journal of Hydrogen Energy**, 39(22):11661-11667, 2014.
- XIA, X.; YANG, Z.; ZHU, Y. Porous carbon-based materials for hydrogen storage: advancement and challenge. **Materials Chemistry A**, 207890:7939-7944, 2015.
- YANG, R. et al. Preparation and N₂, CO₂ and H₂ adsorption of super activated carbon derived from biomass source hemp (*Cannabis sativa* L.) stem. **Microporous and Mesoporous Materials**, 158:108-116, 2012.
- ZHANG, C. et al. Microstructure regulation of super activated carbon from biomass source corncob with enhanced hydrogen uptake. **International Journal of Hydrogen Energy**, 38(22):9243-9250, 2013.
- ZHAO, W. et al. Optimization of activated carbons for hydrogen storage. **International Journal of Hydrogen Energy**, 36(18):11746-11751, 2011.
- ZHAO, W. et al. Synthesis of bamboo-based activated carbons with super-high specific surface area for hydrogen storage. **BioResources**, 12(1):1246-1262, 2017.