



Synthesis of Activated Carbon from Waste Tea by KOH Activation as High Performance Supercapacitors Electrodes

Husnul Hasanah, Syukri and Hermansyah Aziz*

Department of Chemistry, Faculty of Math and Science, Andalas University, Padang, 25163, Indonesia

ABSTRACT

Activated carbon from waste tea (ACt) is prepared via KOH activation under N_2 atmosphere at $800^\circ C$. The results of the ACt shows homogeneous and evenly distributed pores so high specific surface area for achieving high-performance supercapacitor electrodes. The maximum specific surface area of $1451.07 \text{ m}^2/\text{g}$ is observed at the mass ratio ACt and KOH 1:3. As the electrode materials, the ACt exhibit ideal capacitive behaviors in H_2SO_4 electrolyte and the maximum specific capacitance is 162.613 F/g . So the utilization of waste tea for the scalable production of activated carbon for high-performance supercapacitors as low-cost storage devices.

Keywords: Activated carbon; Waste tea; Supercapacitor; Activation; Porous carbon

INTRODUCTION

Supercapacitors are physical energy storage devices where charge transfer occurs without chemical reactions in the energy storage mechanism so it is more environmentally friendly [1]. Supercapacitors have been used extensively in areas such as digital technology, electrical machinery, military equipment, cell phones and electric cars [2]. Supercapacitors consist of three important components such as electrodes, electrolytes, and separators. Electrode materials used for supercapacitors are metal oxides [3], nanocomposites [4], conductive polymers [5] and activated carbon [6]. Recently the electrodes that are often used are activated carbon because metal plates are expensive, rare and their ability as electrodes to store charges is relatively small. More than 80% of supercapacitor electrodes are made of activated carbon [7].

Various studies have been reported on the use of activated carbon from biomass as supercapacitor electrodes such as candlenut shell waste [8], rubber seed shell [9], coconut fiber [10], humic acid from peat soils [11], lignin [12] and palm kernel shell waste [13]. Activated carbon is more beneficial, because the surface area and porosity are high, resistant to high temperatures, large electrical conductivity, low toxicity, high stability and inexpensive [10]. One of the biomass that can be used as a source of porous activated carbon is waste tea. Waste tea is the remnants of tea that has undergone a process of brewing with water. Several studies have been carried out using waste tea as an

organic fertilizer, additives in animal feed [14], absorbents [15] and activated carbon [16]. In this research, waste tea is used because the use of waste tea as a supercapacitor electrode is not optimal and the production costs are low. Theoretically, the selection of waste tea because of its content consists of cellulose 29.42%, lignin 36.94%, ash 4.53%, and extractive 15.22% [17]. The more cellulose, hemicellulose and lignin content, the more activated carbon will be produced [18].

Carbon from waste tea is activated using KOH to obtain activated carbon with high surface area and large pore volume. KOH activator is the most effective agent for forming micropores [9], where KOH can increase the surface area of carbon so that the capacitance value and electrochemical stability of supercapacitor electrodes also increase [19]. Activation using KOH on several carbons gives a high capacitance value, excellent electrochemical stability and has a 98% capability of initial capacitance up to 1000 times the repetition cycle [9]. In this study, different amounts of KOH were used to study the effect of KOH concentrations on pore size, specific surface area, pore volume and specific capacitance values produced by activated carbon of waste tea.

EXPERIMENTAL SECTION

Preparation of activated carbon

Waste tea is collected from local restaurants, then washed with distilled water and dried at room temperature. Samples were roasted at 110°C until constant weight, then furnace at 300°C for 2 hours. The activation process used KOH with a mass ratio of carbon and KOH 1:3, 1:4 and 1:5. Carbon and KOH are stirred until homogeneous for ± 12 hours. Activated carbon is filtered and roasted at 110°C for 1 hour. After that, ACT in the furnace at a temperature of 800°C under a nitrogen atmosphere with a heating rate of 5°C/min for 1.5 hours. The ACT is cooled and washed with distilled water until pH reached 7 to remove inorganic impurities, and then the ACT produced is dried at ± 110°C.

Characterization of activated carbon

Crystallite structure was determined by XRD (PIXcel1D) using Cu K α radiation. The morphology surface area and composition chemical element were investigated using SEM-EDX (S-3400N). The specific surface area was record according to adsorption-desorption isotherms performed by Surface Area Analysis (NOVA 3200e, Quantachrome Instrument). The Brunauer-Emmett-Teller (BET) methods were utilized to calculate the specific surface area. The pore size distribution was derived from the adsorption branch of the corresponding isotherm using the Barret-Joyner-Halenda (BJH).

Electrodes preparation

The activated carbon of waste tea of 0.7 grams was added with 5% PVA to form a paste. After that, the mixture is printed into pellets using a hydraulic press. Then the pellets are dried at 110°C for 24 hours. Two pellets are made and formed in a circle with a diameter of 0.7-0.8 cm. The pellet/electrode is dried at 110°C for 24 hours and then the electrode is weighed in mass and soaked in 1M H₂SO₄ electrolytes for 48 hours.

Electrochemical measurement

The two electrodes are arranged like a sandwich separated by a separator in the middle. Then the two electrodes are enclosed in a stainless steel plate as the current collector. Measurement of electrochemical properties using Cyclic

Voltammetry (CV) with a scan rate of 1 mV/s and a potential range of 0-1 Volt. The specific capacitance value is calculated using the following equation:

$$C_{sp} = \frac{(I_c - I_d)}{s \cdot m} \tag{1}$$

Where C_{sp} is the specific capacitance (F/g), I_c =charge current (A), I_d =discharge current (A), s =scan rate (mV/s) and m =electrodes mass (g).

RESULT AND DISCUSSION

The surface morphology of activated carbon of waste tea (ACt) was analyzed using SEM. Figure 1a shows the pores formed after the activation process with KOH, it can be seen that the resulting pore size distribution is homogeneous and evenly distributed. High porosity in activated carbon of waste tea will increase the surface area and the pores will be a place to store charge on the surface of activated carbon to produce a large specific capacitance value. The results of the XRD analysis on activated carbon of waste tea are shown in Figure 1b. The results of X-ray diffraction patterns at wide peaks at 23° with diffraction peaks (002) and at 44° diffraction peaks (100) following the diffraction of graphitic carbon with amorphous character [16].

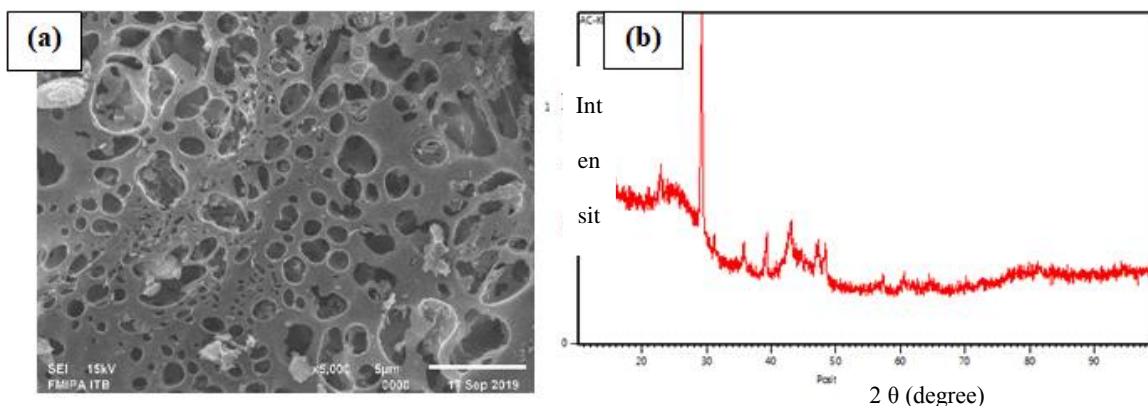


Figure 1. SEM image of ACt (1:3) with 5000 and XRD pattern of ACt (1:3)

The composition of elements contained in ACt was analyzed by EDX. The EDX results in Table 1 show the most elemental composition in ACt is 92.49 % carbon. This is also shown in the diffraction pattern of carbon peaks seen in Figure 2 this indicates that waste tea has been converted to activated carbon. Besides, there is also an oxygen element caused by imperfect carbonization [19,20]. The potassium element may be caused by the KOH activator which is still left behind in the activated carbon of waste tea.

Table 1. Composition of elements content of ACt (1:3)

Element	Weight (%)
C	92.49
O	6.94
K	0.20
Ca	0.37

As mentioned before, waste tea carbon is activated with different amounts of KOH where the ratio is 1:3, 1:4 and 1:5. KOH activation has been widely used to increase specific surface area and improve electrochemical performance. Although KOH activation is often used to produce pores in activated carbon, its activation mechanism is not well known due to the complexity of several variables in the experimental parameters. In general, the reaction between carbon and KOH starts with a solid-solid reaction, then solid-liquid which reduction the potassium compound to metallic K [21,22], oxidation of carbon to carbon oxide and carbonate and other active intermediate reactions [23]. The chemical activation reaction with KOH is mostly the process: $6\text{KOH} + 2\text{C} \rightarrow 2\text{K} + 3\text{H}_2 + 2\text{K}_2\text{CO}_3$, at the higher temperature ($>700^\circ\text{C}$), the K_2CO_3 decomposes to K_2O and CO_2 [24,25].

The specific surface area and pore size of ACt can be determined using the Brunauer Emmet Teller-Barrett Joyner Halenda (BET-BJH) method with nitrogen adsorption and desorption isotherms at a temperature of 77 K. In Figure 2a shows the curve of nitrogen adsorption-desorption isotherms of activated carbon waste tea based on the IUPAC classification is type I showing the presence of micropores and mesopores structures, where the dominant pore structure is micropores. The curves display of the majority of nitrogen adsorption occurred at relatively low pressures ($P/P_0 < 0.2$), indicating the micropores are dominant. Moreover, at the relative medium pressure ($0.2 < P/P_0 < 0.8$) the appearance of small hysteresis indicating the existence of some mesopores. The results show that there are micropores and mesopores on the ACt surface, where micropores provide a space for energy storage and mesopores provide ion transport pathways [2].

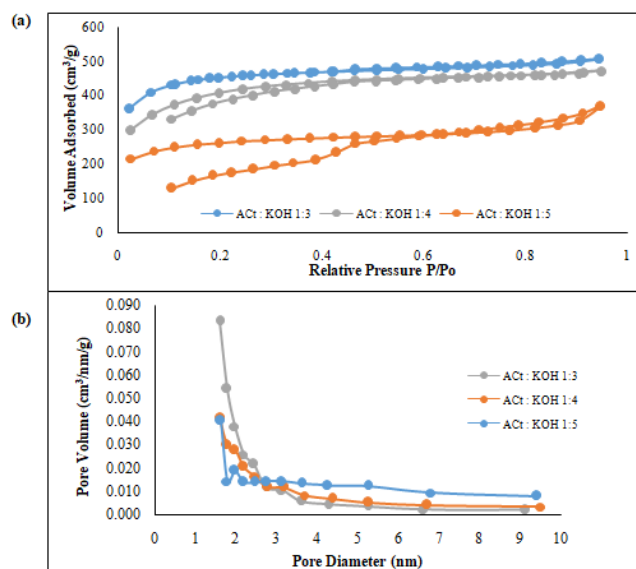


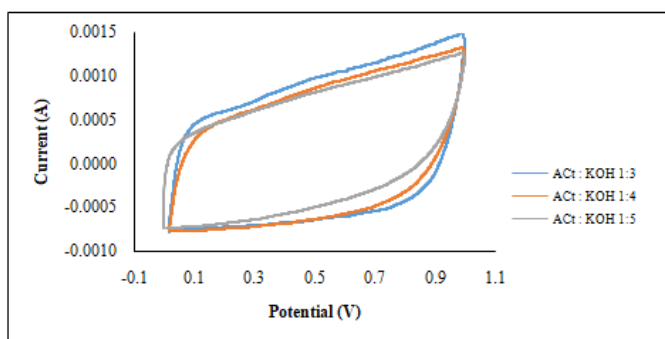
Figure 2. (a) Nitrogen adsorption-desorption isotherms and (b) BJH pore distributions of ACt

Figure 2b shows the pore size distribution calculated by the Barret-Joyner-Halenda (BJH) method. Most pore distributions are found in pore sizes < 2 nm, this means that many micropores structures are formed in the activated carbon of waste tea. And there is also a pore distribution in the pore size between 2-10 nm indicating there are little mesopores in the activated carbon of waste tea. Small pore size and large pore volume are some of the advantages of KOH as an activating agent [16], this can also be seen in Table 2.

Table 2. Specific Surface area, pore volume and specific capacitance of Act

ACt : KOH (% wt)	Specific Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Specific Capacitance (F/g)
1:3	1451.07	0.78645	162.613
1:4	1347.26	0.73250	128
1:5	845.904	0.57360	102

Table 2 shows the highest specific surface area and the largest pore volume of activated carbon of waste tea obtained at a ratio of 1:3 of 1451.07 m²/g and 0.78645 cm³/g. This is because the micropores formed by KOH activation are considerable than 1:4 and 1:5 ratio. The more micropores formed will increase the specific surface area of activated carbon of waste tea. Activated carbon which contains many micropores which produce a large surface area (~1000-2500 m²/g) can produce higher specific capacitance (100-350 F/g) [26]. The high specific surface area of ACt causes a lot of contact with electrolytes to form an electric double layer on the surface of the electrodes to increase the specific capacitance produced. The large pore volume also increases the specific capacitance because a lot of the charge is absorbed and stored on the electrodes. In the ratio of ACt and KOH 1:4 and 1:5, the specific capacitance decreased because more KOH quantity which caused pores damage due to incorporation of smaller pores becomes one bigger pore according to the facts of decreasing specific surface area and pore volume [27].

**Figure 3. The CV curve of ACt at a scan rate of 1 mVs⁻¹**

The electrochemical properties of ACt as supercapacitor electrodes were measured by Cyclic Voltammetry (CV). Figure 3 shows the result of the CV measurement of ACt at a scan rate of 1 mV/s with a potential range of 0 to 1 Volt. The current produced by supercapacitor cells increases significantly and has a wide range seen in Figure 3, this condition shows that ion diffusion from an electrolyte to electrodes surface occurs without resistance. Seen from the voltammogram curves shape, the ratio of ACt and KOH 1:3 has a good symmetrical quasi rectangular shape and produces higher specific capacitance than ACt 1:4 and 1:5. The CV curves of ACt present quasi rectangular shape with scan rate 1 mV/s reveal the ideal storage behavior of supercapacitor. Cyclic voltammogram shows no peaks indicating the supercapacitive character of the electrodes is not from a redox reaction but based on an electrostatic mechanism [28].

CONCLUSIONS

High porous ACt has been successfully produced from waste tea through KOH activation by carbonization under N₂ atmosphere at 800°C. Activation with KOH will increase the specific surface area and pore volume of activated carbon of waste tea so that the value of the capacitance produced is too large. The resulting ACt shows a higher specific surface area and maximum specific capacitance of 1451.07 m²/g and 162.613 F/g at mass ratio ACt and KOH 1:3. This work provides easy, low cost and reliable methods to produce activated carbon from waste tea for high-performance supercapacitors electrodes.

ACKNOWLEDGMENTS

This work was supported by join Physic Laboratory University of Riau and SEM FMIPA ITB Laboratory which provides SEM and EDX data.

REFERENCES

1. A Kumar, S Kriti, B Debmalya. *Int J Sci Eng Technol.* **2013**, 12, 1208-1210.
2. Z Kaiwen, L Yuanyuan, Z Ming, Y Xi, Z Mengyan, S Ling, C Jue. *J Power Sources.* **2017**, 366, 270-277.
3. CS Ferreira, RR Passos, LA Pocrifka. *J Power Sources.* **2014**, 271, 104-107.
4. R Memori, I Fery, A Mikrajuddin, Khairurrijal. *J Mat Sci Forum.* **2013**, 737, 191-196.
5. R Memori, I Fery, A Mikrajuddin, Khairurrijal. *Electrochem Sci.* **2014**, 9, 4251-4256.
6. A Hermansyah, NT Olly, A Admin, Syukri, AP Yola. *Jurnal Zarah.* **2017**, 2, 1-6.
7. Z Liu, Z Zhu, J Dai, Y Yan. *J Chem Pub Soc Europe.* **2018**, 3, 5726-5732.
8. M Kwiatkowski, E Broniek. *Colloids Surf.* **2017**, 529, 443-453.
9. T Pagketananga, A Artnaseawa, P Wongwichaa, M Thabuota. *Energy Procedia.* **2015**, 79, 651-656.
10. L Yin, Y Chen. *Material and Design.* **2015**, 111, 44-50.
11. ZJ Qiao, MM Chen. *Bioresource Technol.* **2014**, 163, 386-289.
12. B Yu, Z Chang. *Materials Chem Physic.* **2016**, 181, 187-193.
13. NT Olly, Syukri, A Hermansyah. *Earth Environ Sci.* **2018**, 209, 012-021.
14. M Kondo, M Nakano, A Kaneko, H Agata, K Kita, H Yokda. *Asian-Australas J Anim Sci.* **2004**, 17, 960-966.
15. AH Mahvi, D Naghypour, F Vaezi, S Nazmara. *Am J App Sci.* **2005**, 2, 372-375.
16. C Peng, X Yan, R Wang, J Lang, Y Ou, Q Xue. *Electrochimica Acta.* **2013**, 87, 401-408.
17. A Tutus, Y Kazaskeroglu, M Cicekler. *Bio Resources.* **2015**, 10, 5407-5416.
18. PG Garcia. *Renewable Sustainable Energy Rev.* **2018**, 82, 1393-1414.
19. N Kamikuri, Y Hamasuna, D Tashima, M Fukuma, S Kumagai, JD Madden. *Int J Innov Res Sci Eng Technol.* **2014**, 3, 492-501.
20. H Jankowski, A Swiatkowski, J Choma. *Ellis Horwood, London.* **1991**, 31-40.
21. T Otowa, R Tanibata, M Itoh. *Gas Sep Purif.* **1993**, 7, 241-245.
22. D Lozano-Castello, JM Calo, D Cazorla-Amoros, A Linares-Solano. *Carbon.* **2007**, 45, 2529-2536.
23. W Jiacheng, K Stefan. *J Mat Chem.* **2012**, 22, 23710-23725.

24. M Sevilla, AB Fuertes. *Chem Sus Chem.* **2016**, 9, 1880-1888.
25. V Jimenez, P Sanchez, JL Valverde, A Romero. *J Colloid Interface Sci.* **2009**, 336, 712-722.
26. A Ghosh, YH Lee. *Chem Sus Chem.* **2012**, 5, 480-499.
27. B Khalid, Q Meng, R Akram, B Cao. *Desalination Water Treat.* **2014**, 57, 2195-2202.
28. R Farma, M Derama, T Awitdrus, R Omar, JG Manjunatha, MM Ishak, NH Basri, BNM Dollah. *Int J Electrochem Sci.* **2012**, 8, 257-273.