Characteristics of Corncob-Originated Activated Carbon Using Two Different Chemical Agent

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Abstract. The research and development of biomass-based activated carbon (AC) has attracted much attention from researchers due to the abundant resource of biomass, including corncob waste. The urgency to find alternative and innovative applications for simple, inexpensive carbon material can be obtained by synthesizing the corncob waste which is abundant renewable resource and suitable for carbon properties. The use of chemical agent during activation process is of important to produce the desired AC, including high surface area and excellent electrical conductivity. Among the various chemical agents, KOH and ZnCl₂ have been widely applied for synthesizing AC. This study aims to find out the characteristics of corncob-originated activated carbon (CAC) using these two chemical agents. Step by step of activating carbon from corncob will be determined briefly. Corncob was dried and chopped. Then it was carbonized. After that, the carbon result was soaked in each chemical agent solution, KOH and ZnCl₂, in different molarity for carbon chemical activation. For physical activation, impregnated carbon was carbonized again in high temperature under inert gas atmosphere until AC was obtained. We employed scanning electron microscopy (SEM), X-Ray diffraction (XRD), and Raman Spectroscopy measurement to characterize the CAC samples. The results showed that the application of KOH and ZnCl₂ at a different optimized process parameters exhibited the different results of surface morphology, structures, and crystallite size. The crystallite size of the activated carbon using different chemical activating agents with varied concentrations is diverse enough. The XRD data revealed the average crystallite size of carbon with KOH as the activator is ~45 nm in three different conditions. However, in the case of ZnCl₂ as the activating agent, it shows the average size of ~65 nm. This number is significantly higher than the activated carbon impregnated with KOH. Visual observation of SEM images gives an impression on the carbon pore where CACK12 possess the highest pores among those analytes. The synthesized corncob activated carbon can be used in many functional application such as energy storage materials, agriculture, and adsorbents in industrial and environmental sectors.

Keywords: activated carbon, corncob, chemical Agent, KOH, ZnCl₂.
1. Introduction

Due to abundant benefit, development of activated carbons (AC) which have large surface area and high microporosity is becoming a hot topic for many researcher at present. CO2 adsorbents [1, 2], electrode materials for energy storage [3-7] and catalyst [8] are some examples of AC's benefits. Many commercial AC are produced from non-eco-friendly materials with difficult and complicated process, also high cost production. The research and development of simple, low cost [9], and biomass based activated carbon [4, 6, 10] get many interest from researcher. Several studies have reported biomass based carbon such as coconut shell [11], sunflower seed [12], palm kernel shell [1], fish waste [13], etc. One of potential biomass that can be turned into active carbon is corncob. Based on data from the Central Statistics Agency (Badan Pusat Statistik-BPS), corncob waste in Indonesia reached 7.5 million tons in 2014. During this time, corncob in Indonesia is only used as fodder. Through this study expected to increase the added value of corncob.

In this study, we demonstrated a simply way to produce a biomass based activated carbon that derived from corncob. The previous studies, researcher use only the innermost part of corncob [14], but in this experiment we used the whole part of corncob. Various strategies have been developed to fabricate AC which has high surface area and great conductivity, one of which is chemical or physical activation methods.

First physical activation aims to remove vaporous substance that can worsen char performance. In chemical activation, the char is mixed with a chemical activating agent such as KOH [15], NaOH [16], HCl [10], ZnCl$_2$ [16-18] to eliminate the tar content and expand the pore size. Selection of chemical agent important because some organic matter can only make a bonding and reaction in certain chemicals to form excellent activated carbon.

![Figure 1. Schematic Diagram of Activated Carbon Preparation](image)

After completion of chemical immersion, it is followed by carbonization under an inert gas at high temperature ranging 300-700°C [19] then washed to get neutralized charcoal. Carbonization temperature, carbonization time, gas flow rate, and impregnation ratio are crucial parameters in the AC surface area and pore formation [10, 19, 20]. Among chemical activation method, ZnCl$_2$ and KOH are widely used for activating carbon because ZnCl$_2$ and KOH can develop the pore size distribution, volume, and surface area with efficient and flexible method [2, 3]. This work aimed at characterizing AC with chemical activator KOH and ZnCl$_2$. Effect of various C: Solutions mass ratio also investigated to find the optimum activations.

2. Experimental methods

2.1. Active carbon preparation

Preparation of active carbon including three processes; pre-carbonization process, physical activation, and chemical activation. The corncob were sundried then grinded into powder. Then, the powder were
carbonized in a horizontal tube furnace under argon flow atmosphere of 200 cc / min, the temperature was increased until 600°C for 1h and held in 600°C for 2h. After turning to room temperature, carbonized sample was mixed in chemical solution by magnetic stirrer for chemical activation process. Chemical solution that used in this experiment was ZnCl₂ and KOH solution with different mass ratio for variations. The char: activating agent mass ratio chosen in this study were 1: 2, 1: 3, and 1: 4. The bigger mass of chemical agent makes the molarity of chemical solution. The mixture was dried in oven for 12h then furnaced again under Ar flow of 300cc / min with increasing temperature 400°C for 1h and held in 400°C for 1h. The corncob originated activated carbon (CAC) obtained from ZnCl₂ chemical agents were washed with aquadest and CAC obtained from KOH solutions were washed with HCl and aquadest to neutralized the CAC. The washed CAC then dried in oven for 12h until final CAC were obtained. The CAC produced from ZnCl₂ activation denoted as CACZ1₂ (1:2), CACZ1₃ (1:3), and CACZ1₄ (1:4). The CAC produced from KOH activation denoted as CACK1₂ (1:2), CACK1₃ (1:3), and CACK1₄ (1:4).

2.2. Material Characterization

2.2.1. Scanning Electron Microscopy (SEM). The morphologies and microstructures of the samples were determined using scanning electron microscopy (NOVA-SEM, FEI Company). The operating voltage was 10 kV, and the magnifications of the images were 5000 and 10.000.

2.2.2. X-Ray Diffraction (XRD). X-ray diffraction analysis is used to exhibit the structures and composition of the samples. The crystallite size can be measured by XRD. X-ray diffraction (XRD) patterns were obtained on a Rigaku using Cu Kα radiation (with measurement range 10-80 degree, λ=1.540598 Å). Scan were recorded with scanning rate 0.04° s⁻¹.

2.2.3. Raman Spectroscopy. Raman spectra were recorded by micro Raman Spectrometer from Renishaw Company at an excitation wavelength of 532 nm.

3. Results and discussion

3.1. SEM Analysis

Error! Reference source not found. shows the SEM photographs of activated carbon from corncob that applying KOH and ZnCl₂ activation with different mass ratio. The pore width of CACK1₂ is around 5.71 µm, CACK1₃ is 7.43 µm, and CACK1₄ is 8 µm. While the pore size of carbon impregnated by ZnCl₂ as follows, CACZ1₂ is around 11.71 µm, CACZ1₃ is 10.85 µm, and CACZ1₄ is 6.57 µm. This result shows that all of the samples has the macroporous morphological structures as the pore size is larger than 50 nm. CACK1₂ has the clearest surface morphology like a coral with distributed pores, indicating the homogeneous cover of chemical agents. While CACZ1₄ displays like solid ball with small pores, indicating that the processing method faced some problems. The hole and granular of carbon displayed in the picture were the result of activation both physical and chemical activation as reported in other research [15]. It can be inferred that various pore size of carbon are depending on the impregnation ratio. It was observed from Fig.2 that the higher KOH molarity employed, the greater pore size of carbon resulted. Contrast with KOH activation, SEM photograph of ZnCl₂ shows that the smaller ZnCl₂ molarity, the greater CAC pore size obtained.
Figure 2. SEM Images of (a) CACK12, (b) CACK13, (c) CACK14, (d) CACZ12, (e) CACZ13, and (f) CACZ14

3.2. XRD Analysis
Giving a better understanding about the carbon structure, XRD test has been conducted to analyze more deeply about the structural materials using software Match! version 3.0. The plotting XRD data is provided in the Fig. 2. It is clearly indicated that broad peaks are centered at $2\theta = \sim 28^\circ$ and $2\theta = \sim 40^\circ$ that belongs to biomass-based carbon peaks. Based on our calculations, the structure of obtained carbon turns out to be amorphous that is reflected by the miller indices of (002) and (101) respectively [12], [14]. This is supported by our next peak observation at $\sim 28^\circ$ is due to (002) lattice plane of typical graphite structure of carbon-black. The XRD graph also shows that CACKs exhibited the uniform pattern changes. The peaks represent a graphitic crystal structure of the samples. Nevertheless, some other peaks were still present, associated with the chemical agents that might be there due to incomplete removal during washing processes to neutralize the yielded activated carbon.

Figure 3. SEM Images of (a) CACK12, (b) CACK13, (c) CACK14, (d) CACZ12, (e) CACZ13, and (f) CACZ14
To further calculate the crystallite size we use the Scherrer’s equation as following:

\[ B = \frac{0.9 \times \lambda}{d \times \cos \Theta} \]  

(1)

where \( \lambda \): wavelength (1.54060 Å of Cu Kα1), \( \Theta \): \( 2\Theta/2 \); \( d \): Full Width at Half Maximum (FWHM) intensity of the peak (rad); Angle’s unit conversion (degree to rad): \( \text{Rad} = \pi \times \text{degree}/180 \).

The crystallite size of CACK12 is 51.21 nm, CACK13 is 41 nm, and CACK14 is 40.96 nm. While the crystallite size of carbon impregnated by ZnCl₂ as follows, CACZ12 is around 82 nm, CACZ13 is 66.8 nm, and CACZ14 is 42.65 nm. The absence of C-atom in Match! analysis determine that the carbon still make bonding with other compound.

3.3. Raman Spectra Analysis

Using OriginPro Software, the Raman spectra are deconvoluted into two peaks as shown in Error! Reference source not found.. From the graph we can obtain the value of D-Band and G-Band. D-Band is corresponding to an irregular mode or defects on \( A_{1g} \) Symmetry. Defects are required to disseminate elastically for the momentum of conservation is fulfilled, observed on 1330 and 1360 cm\(^{-1}\). While G-band is a tangential shear mode of the carbon atom corresponding to the stretching mode in the graphite plane, show the ideal mode of graphite on \( E_{2g} \) Symmetry, which is observed on 1580 cm\(^{-1}\). Table 1 show the measurement of G-band and D-band. The dominant peak of D-band than G-Band indicates the presence of amorphous carbon in the sample.

![Figure 4. Raman Spectra of (a) CACK12, (b) CACK13, (c) CACK14, (d) CACZ12, (e) CACZ13, and (f) CACZ14](image)

Quality of the sample is evaluated using intensity band ratio \( I_D/I_G \). For high quality samples without defects and without amorphous carbon ratio is usually less than 2%. The samples intensity band ratio has been calculated as showed Table 1. Intensity band ratio is also used for assessing the graphitic in-plane microcrystalline size of carbon (\( L_a \)), which can be formulated [3]:

\[ \frac{I_D}{I_G} = \frac{C_2}{L_a} \]  

(2)

Where \( C_2 \) is 4.4 nm.
Comparing $L_a$, values to the XRD crystal size calculation ($1\,\text{Å} = 0.1\,\text{nm}$), a little disparity has appeared, which CACK14 has the biggest distinction (2.01 nm). The CACZ12 precursor has the most similar crystal size, with the distinction is only 0.01 nm. This discrepancy can occur because the inaccuracy possibility of XRD graph analysis and $L_a$ calculation.

### Table 1. Measurement of G-band and D-band

| Samples  | D-Band | G-Band | $I_D/I_G$ | $L_a$ (nm) |
|----------|--------|--------|-----------|------------|
| CACK12   | 1361.85| 1579.49| 1.46      | 3.01       |
| CACK13   | 1364.38| 1586.15| 2.19      | 2.01       |
| CACK14   | 1369.02| 1586.33| 1.61      | 2.73       |
| CACZ12   | 1380.4 | 1592.31| 3.03      | 1.45       |
| CACZ13   | 1364.89| 1587.19| 2.27      | 1.98       |
| CACZ14   | 1357.86| 1450.22| 8.81      | 0.49       |

### 4. Conclusion

The study of characterization of corncob-originated activated carbon (CAC) using two different chemical agents has been carried out. Among two chemical agents, KOH provides the best performance in terms of surface morphology, meanwhile the ZnCl$_2$ has the best impact in terms of structure and crystallite size. It can be concluded that ZnCl$_2$ is more suitable to be an activator agent for corncob biomass than KOH. Variation in mass ratio also generate diversity in CAC properties. It becomes a great challenge to find optimum chemical agent mixture and method to obtain excellent performance of activated carbon.

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### References

[1] N. A. Rashidi and S. Yusup, "Potential of palm kernel shell as activated carbon precursors through single stage activation technique for carbon dioxide adsorption," *Journal of Cleaner Production*, vol. 168, pp. 474-486, 2017/12/01/ 2017.

[2] K. Chomiak, S. Gryglewicz, K. Kierzek, and J. Machnikowski, "Optimizing the properties of granular walnut-shell based KOH activated carbons for carbon dioxide adsorption," *Journal of CO2 Utilization*, vol. 21, pp. 436-443, 2017/10/01/ 2017.

[3] Z. J. Zhang, C. Dong, X. Y. Ding, and Y. K. Xia, "A generalized ZnCl$_2$ activation method to produce nitrogen-containing nanoporous carbon materials for supercapacitor applications," *Journal of Alloys and Compounds*, vol. 636, pp. 275-281, 2015/07/05/ 2015.

[4] X. Xu, Z. Meng, X. Zhu, S. Zhang, and W.-Q. Han, "Biomass carbon composited FeS2 as cathode materials for high-rate rechargeable lithium-ion battery," *Journal of Power Sources*, vol. 380, pp. 12-17, 2018/03/15/ 2018.

[5] K. Ö. Köse, B. Pişkin, and M. K. Aydnol, "Chemical and structural optimization of ZnCl$_2$ activated carbons via high temperature CO2 treatment for EDLC applications," *International Journal of Hydrogen Energy*, 2018/04/24/ 2018.

[6] F. Sun *et al.*, "Converting biomass waste into microporous carbon with simultaneously high surface area and carbon purity as advanced electrochemical energy storage materials," *Applied Surface Science*, vol. 436, pp. 486-494, 2018/04/01/ 2018.
[7] Q. Abbas, M. Mirzaeian, A. A. Ogwu, M. Mazur, and D. Gibson, "Effect of physical activation/surface functional groups on wettability and electrochemical performance of carbon/activated carbon aerogels based electrode materials for electrochemical capacitors," *International Journal of Hydrogen Energy*, 2018/05/30/ 2018.

[8] T. Tsoncheva *et al*., "Activated carbon from Bulgarian peach stones as a support of catalysts for methanol decomposition," *Biomass and Bioenergy*, vol. 109, pp. 135-146, 2018/02/01/ 2018.

[9] G. G. Stavropoulos and A. A. Zabaniotou, "Minimizing activated carbons production cost," *Fuel Processing Technology*, vol. 90, no. 7, pp. 952-957, 2009/07/01/ 2009.

[10] M. Danish and T. Ahmad, "A review on utilization of wood biomass as a sustainable precursor for activated carbon production and application," *Renewable and Sustainable Energy Reviews*, vol. 87, pp. 1-21, 2018/05/01/ 2018.

[11] K. Sun *et al*., "Microporous activated carbons from coconut shells produced by self-activation using the pyrolysis gases produced from them, that have an excellent electric double layer performance," *New Carbon Materials*, vol. 32, no. 5, pp. 451-459, 2017/10/01/ 2017.

[12] U. Morali, H. Demiral, and S. Şensöz, "Optimization of activated carbon production from sunflower seed extracted meal: Taguchi design of experiment approach and analysis of variance," *Journal of Cleaner Production*, vol. 189, pp. 602-611, 2018/07/10/ 2018.

[13] A. B. Fadhil, A. I. Ahmed, and H. A. Salih, "Production of liquid fuels and activated carbons from fish waste," *Fuel*, vol. 187, pp. 435-445, 2017/01/01/ 2017.

[14] J. Guo, J. Zhang, F. Jiang, S. Zhao, Q. Su, and G. Du, "Microporous carbon nanosheets derived from corn cobs for lithium–sulfur batteries," *Electrochimica Acta*, vol. 176, pp. 853-860, 2015/09/10/ 2015.

[15] S. Li, K. Han, J. Li, M. Li, and C. Lu, "Preparation and characterization of super activated carbon produced from gulfweed by KOH activation," *Microporous and Mesoporous Materials*, vol. 243, pp. 291-300, 2017/05/01/ 2017.

[16] M. Kılıç, E. Apaydın-Varol, and A. E. Pütün, "Preparation and surface characterization of activated carbons from Euphorbia rigida by chemical activation with ZnCl2, K2CO3, NaOH and H3PO4," *Applied Surface Science*, vol. 261, pp. 247-254, 2012/11/15/ 2012.

[17] R. G. Pereira *et al*., "Preparation of activated carbons from cocoa shells and siriguela seeds using H3PO4 and ZnCl2 as activating agents for BSA and a-lactalbumin adsorption," *Fuel Processing Technology*, vol. 126, pp. 476-486, 2014/10/01/ 2014.

[18] S. Yorgun, N. Vural, and H. Demiral, "Preparation of high-surface area activated carbons from Paulownia wood by ZnCl2 activation," *Microporous and Mesoporous Materials*, vol. 122, no. 1, pp. 189-194, 2009/06/01/ 2009.

[19] O. Üner and Y. Bayrak, "The effect of carbonization temperature, carbonization time and impregnation ratio on the properties of activated carbon produced from Arundo donax," *Microporous and Mesoporous Materials*, vol. 268, pp. 225-234, 2018/09/15/ 2018.

[20] Ş. Karadirek and H. Okay, "Statistical modeling of activated carbon production from spent mushroom compost," *Journal of Industrial and Engineering Chemistry*, vol. 63, pp. 340-347, 2018/07/25/ 2018.