The influence of activator type and temperature activation on the specific surface of corncob waste adsorbent

Novia Rachmawati, Muhammad Mujiburohman

Chemical Engineering Department, Faculty of Engineering, Universitas Muhammadiyah Surakarta. Jl. A. Yani Tromol Pos I Pabelan, Kartosuro, Sukoharjo, Surakarta-Indonesia 57162

E-mail: mmujiburohman@ums.ac.id

Abstract. Activated carbon is widely used in various applications. It can be produced from natural sources having carbon content including corncob waste. This study aims to make activated carbon from the corncob waste. The effect of types of activators and activation temperature on the specific surface of the activated carbon was investigated. The experimental stages involved preparation, carbonization, activation, and sample analysis. During activation, the types of activators and temperature activation were varied, i.e. HNO$_3$, HCl, H$_2$SO$_4$, NaOH, all with concentration of 10% (mass), and variations in temperature of 70$^\circ$C, 90$^\circ$C, 110$^\circ$C. The specific surface of activated carbon was determined with the methylene blue adsorption method using UV-Vis spectrophotometer. The results showed that the activation using 10% NaOH at a temperature of 110$^\circ$C had the highest specific surface, i.e. 21.876 m$^2$/g.

1. Introduction

Absorption is a separation method particularly used to remove small amount of particles from a fluid phase. Adsorption is driven by the attractions between molecules due to the existence of force field on a solid surface (adsorbent) [1]. Adsorption has advantages over other processes; among the advantages are able to produce high quality processed waste and save process costs [2].

One of adsorbents frequently applied in practical applications is activated carbon. Activated carbon is carbon that has been activated, so it has a more porous structure with a surface area ranging from 400-1400 m$^2$/g [3]. Activated carbon is widely used in separation processes and catalyst technologies, such as pollutant removal, gas separation, catalyst support, electrolysis cell electrode materials, and wastewater treatment. Activated carbon is able to remove most of the organic contaminants because it has a high surface area and porosity [4]. The widely used activated carbon as adsorbent is due to easy manufacture, low cost, high adsorption capacity [5].

The characteristics of activated carbon required for adsorption include having a large adsorbent surface area, having a large adsorption capacity, having good resistance to shocks, and no significant volume changes during the adsorption process [6]. Activated carbon is made by immersing carbon in an activator solution, where this activator will dissolve carbon impurities and produce pores. The types of activators that are widely used include NaCl, ZnCl$_2$, H$_2$SO$_4$, HNO$_3$, HCl, and H$_2$SO$_4$.
H₃PO₄, Ca(OCl)₂, and NaOH [7]. The operating conditions in the adsorbent preparation can be optimized to obtain the optimum pore size. The increase in the pore size of carbon reflects an increase in the surface area of the carbon [8].

Natural materials with high carbon content and low inorganic are potential as raw materials for activated carbon. Activated carbon from durian skin has been made by [9] with KOH and NaOH activators, and obtained the KOH activator more efficiently than NaOH. [10] showed that carbon activation using NaOH activator resulted in a better adsorption capacity than H₂SO₄. Meanwhile, [11] showed that H₂SO₄ activator was better than using HCl activator.

As a matter of fact, the need for activated carbon in Indonesia is still high because its use is increasingly widespread in various sectors. According to the BPS report, the amount of activated carbon imports from 2009-2012 has increased by around 37.23%, and currently Indonesia is still importing activated carbon to meet the needs. Due to the abundant natural resources, Indonesia is very potential to become an activated carbon producer. One of the prospective natural materials as the raw material of activated carbon is corncob waste. According to the Indonesia’s Central Statistics Agency (BPS), in 2014 the production of corn in Indonesia reached 19.0 million tons, and increased by 52.11% at the end of 2017. The increase in corn production has implications for the increase in the waste produced, especially corncob. Corncobs, which are attached to corn kernels, are potential to act as activated charcoal (carbon) because they are composed of cellulose (41%), hemicellulose (36%), lignin (6%), and other common compounds in plants [12].

The present work aims to study the manufacture of activated carbon from the corncob waste. The effect of activator type and activation temperature on the main characteristic of activated carbon produced, i.e. specific surface, was investigated.

2. Method
The materials used were corncob, acid activators (HNO₃, HCl, H₂SO₄), base activator (NaOH), methylene blue, and aquadest. All these chemical materials were provided by the Laboratory of Chemical Engineering, Universitas Muhammadiyah Surakarta. The main equipments consist of furnace, screen 60 mesh, desicator analytical balance, hot plate, magnetic stirrer, filter paper, and spectrometer UV-Vis; all these apparatus were also kindly provided by the same laboratory.

The experiments involved four main stages, i.e. sample preparation, carbonization, activation, and sample analysis. In the sample preparation, the corncobs were washed under the flowing water until clean and were dried in the sun until they were completely dry. The dry corncobs were then put in a furnace at 400°C for 1 hour to perform carbonization. Furthermore, the charcoal formed was crushed and sieved with a 60 mesh screen. A total of 10 g of charcoal was soaked using various activators (10% HNO₃, 10% HCl, 10% H₂SO₄, and 10% NaOH) for 24 hours. Then, the mixture was filtered and neutralized to a neutral pH (pH 7) and was put in the oven for 3 hours at temperature variations of 70, 90, and 110°C.

The surface area of the activated carbon was determined using the methylene blue adsorption method, initiated with the determination of the maximum wavelength of methylene blue (C₁₆H₁₈N₃) in the range of 650-700 nm using a UV-Vis spectrophotometer [13]. Methylene blue standard solution was prepared by varying the concentration of methylene blue (1, 2, 3, 4, 5 ppm), and the absorbance of each concentration was measured using a UV-Vis spectrophotometer at a wavelength of 664 nm. The relationship between the methylene blue concentration and the absorbance was correlated by means of regression, and the equation obtained was used to determine the methylene blue concentration in the adsorption test to determine the specific surface. The specific surface (S) of activated carbon was calculated using the following formula [9]:

\[ S = \frac{W_{ads} \times N \times a}{M_r} \]  

(1)
where $W_{ads}$ is the mass of adsorbate (methylene blue) adsorbed onto the activated carbon, and $N$ is Avogadro number ($6.022 \times 10^{23} \text{ mole}^{-1}$). $M_r$ and $a$ are the molecular weight of methylene blue (320.5 g/mole) and the area covered by a methylene blue molecule ($197 \times 10^{-20} \text{ m}^2$), respectively.

3. Results and Discussion

3.1. Effect of Activation Temperature

The effect of activation temperature on the specific surface of the activated carbon of corncob is shown in Table 1. It is clear that the increase in activation temperatures increases the specific surface of activated carbon. Generally speaking, the solubility of solid materials in liquid solvents increases as the temperature increases. The more particles dissolved from the carbon, the more pores are formed in the carbon.

| Activation Temperature ($^\circ$C) | Specific Surface (m$^2$/g) |
|-----------------------------------|-----------------------------|
| 70                                | 10.739                      |
| 90                                | 21.601                      |
| 110                               | 21.709                      |

3.2. Effect of Type of Activator

Table 2 presents the effect of type of activator on the specific surface of the activated carbon of corncob.

| Type of Activator | Specific Surface (m$^2$/g) |
|-------------------|----------------------------|
| HNO$_3$           | 19.481                     |
| HCl               | 21.709                     |
| H$_2$SO$_4$       | 21.733                     |
| NaOH              | 21.876                     |

It can be seen that NaOH is the most effective activator for activating the carbon from the corncob waste, i.e. 21.876 m$^2$/g. NaOH is able to degrade the structure of lignin, heicellulose, and the pores become more open so that they have better absorption [10]. Meanwhile, H$_2$SO$_4$ activation is better than activation with HCl or HNO$_3$, because sulfuric acid has 2H$^+$ which is able to encourage non-volatile substances in the pores so that the pores will be bigger and produce a larger surface area [11]. The specific surface area resulted from this study is higher than the surface area of banana stem adsorbent conducted by [14], i.e. 3.4559 m$^2$/g. However, it is still lower than the requirement (500-1500 m$^2$/g, SII No. 0258-88).

4. Conclusion

Activated carbon from the corncob waste can be made. Increasing the activation temperature increases the specific surface. NaOH is known as the best activator in comparison with acid activators (H$_2$SO$_4$, HCl, HNO$_3$). Within the ranges of studied variables, the highest specific surface of activated carbon of corncob was obtained at 110$^\circ$C, 10% NaOH, i.e. 21.876 m$^2$/g.
References

[1] Ościk, J. 1982. Adsorption. John Wiley & Sons. New York.

[2] Garcia, A.M., Corzo, M.G., Dominguez, M.A., Franco, M.A., dan Naharro, J.M. 2016. Study of the Adsorption and Electroadsorption Process of Cu (II) Ions within Thermally and Chemically Modified Activated Carbon. Journal of Hazardous Materials, 328, 46-55.

[3] Mutiara, T., Fajri, R., Nurjannah, I. (2016) ‘Karakterisasi Karbon Aktif dari Serbuk Kayu Nangka Limbah Industri Penggergajian dan Evaluasi Kapasitas Penyerapan dengan Methylene Blue Number’ Tenoin, 22(6), 452–460.

[4] Yue, Z.R., Wang, J.W., Economy, J. 2013. Pore control of ZnCl2-activated cellulose on fiberglass mats for removal of humic acid from water. Mater, 90, 8–10.

[5] Sahira, J., Mandira, A., Prasad, P.B., dan Ram, P.R. 2013. Effect of Activating Agents on the Activated Carbons Prepared from Lapsi Seed Stone. Research Journal of Chemical Sciences, 3(5), 19-24.

[6] Darmanasyah., Simparmin, G., Ardiana, L., dan Saputra, H. 2016. Mesopori MCM-41 sebagai Adsorben : Kajian Kinetika dan Isoterm Adsorpsi Limbah Cair Tapioka. Jurnal Rekayasa Kimia dan Lingkungan, 11(1), 10-16.

[7] Setiawati, E., Suroto, S. 2010. Pengaruh Bahan Aktivator pada Pembuatan Karbon Aktif Tempurung Kelapa, Jurnal Riset Industri Hasil Hutan, 2(1), p. 21. doi: 10.24111/jrihh.v2i1.911.

[8] Abechi, S.E., Gimba, C.E., Uzairu, A., dan Dallatu, Y.A. 2013. Preparation and Characterization of Activated Carbon from Palm Kernel Shell by Chemical Activation. Research Journal of Chemical Sciences, 3(7), 54-61.

[9] Hanum, F., Gultom, R.J., dan Simanjuntak, M. 2017. Adsorpsi Zat Warna Metilen Biru dengan Karbon Aktif dari Kulit Durian menggunakan KOH dan NaOH sebagai Aktivator. Jurnal Teknik Kimia, 6(1), 49-55.

[10] Zaini, H., dan Sami, M. 2016. Kinetika Adsorpsi Pb(II) dalam Air Limbah Laboratorium Kima menggunakan Sistem Kolom dengan Bioadsorben Kulit Kacang Tanah. Seminar Naional Sains dan Teknologi, Jakarta: 8 November 2016. 1-8.

[11] Pujiono, F.E., dan Mulyati. 2017. Potensi Karbon Aktif dari Limbah Pertanian sebagai Material Pengolahan Air Limbah. Jurnal Wiyata, 1(1), 37-45.

[12] Komariah, N.L., Aldiat, S., dan Sari, N.V. 2013. Pembuatan Karbon Aktif Dari Bonggol Jagung Manis (Zea Mays Saccharata Sturt) dan Aplikasinya Pada Pemurnian Air Rawa. Jurnal Teknik Kimia, 19(3), 1-8.

[13] Huda, T., Yuliantiningtyas, T.K. 2018. Kajian Adsorpsi Methylene Blue menggunakan Selulosa dari Alang-Alang. Indonesian Journal of Chemical Analysis, 1(1), 09-19.

[14] Widihati, I.A.G., Suastuti, Ng.A.M.D.A., Nirmalasari, M.A.Y. 2012. Studi Kinetika Adsorpsi Larutan Ion Logam Kromium (Cr) Menggunakan Arang Batang Pisang (Musa paradisiaca). Jurnal Kimia. Vol. 6 No. 1.