Preparation of Activated Carbon from Corn Cobs using $ZnCl_2$ as Chemical Agent

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ABSTRACT

The production of porous carbon from waste biomass materials is crucial for environmental remediation. Carbon's pore structure and characteristics are directly tied to the biomass type and carbonization conditions. This study involved the preparation of various porous, biomass-activated carbon (AC) materials employing Zinc chloride as the pore-forming agent. The impact of the prepared carbon diameter and the activated agent on the produced carbon's surface area and pore size was studied. Three carbon diameters of 0.2, 0.4, and 0.6 mm were determined for the study. It was found that the best surface area and pore size before and after activation were obtained when the carbon diameter was 0.4 mm, and the surface area was 245 m^2/g.

Keywords: Activated carbon, biomass, $ZnCl_2$.

1. Introduction

Activated carbon (AC) is one type of inexpensive adsorbent and one of the most widespread adsorbents. It is identified with a high surface area and increment absorbs impurities. Because activated carbon has a high specific surface area and an excellent pore size distribution, it is particularly well suited for use as an adsorbent. As a result, activated carbon is frequently employed to decrease air and water pollution [1]. For the most efficient manufacture of activated carbon, natural ingredients or biomass derived from agricultural waste should be used as the raw material source. Utilizing biomass derived from agricultural and industrial waste as an adsorbent is not only budget-friendly but also kind to the environment. The biomass, including green coke [2] and lignocellulose-containing materials like almond shell [3], rubber wood [4], argan shell [5] (Argania spinosa), tobacco [6], pineapple peel [7], oil palm empty fruit bunches [8,9], and Terminalia catappa fruit shells [10], are proven precursor materials for activated carbon production. [10].

The carbon pore structure obtained from carbon materials and the carbonization procedure greatly influence the adsorption efficiency. Corn cobs were utilized to make activated carbon because they were abundant and inexpensive. The porous structure and molecular characteristics of the carbon surface could be influenced by the chemical activation process.

Activation agents such as KOH [11], H2SO4 [12], HNO3 [13], and CaCO3 [14–16] have been utilized for synthesizing biomass carbon. $ZnCl_2$ has recently gained a lot of notoriety for its use as a high-performance chemical activation agent in producing porous carbon products from a wide range of biomass. As a Lewis acid, $ZnCl_2$ could be utilized as a dehydrating agent to specifically eliminate O and H from biomass, thereby limiting creosote formation and enhancing the creation of structural porosity and high surface area [17,18]. $ZnCl_2$ has been employed to activate solid olive wastes for generating AC with a tenfold greater specific surface area (1,480 m^2/g) and enhanced nitrate adsorption capacity (5.5 mg/g) [19].

The present investigation involved preparing activated carbons derived from porous corn cobs, utilizing $ZnCl_2$ (activating agent). The effect of using different diameters of activated carbon has been studied. Tests have been carried out to determine the prepared activated carbon's surface area and pore size before and after chemical activation using zinc chloride.

2. Materials and Experimental Methods

2.1. Materials

The obtained dry anhydrous zinc chlorides were utilized for the activation process without additional purification. Distilled water was utilized throughout.

2.2. Activated carbon preparation

Corn cobs were used as the primary carbon source in the preparation of porous activated carbon adsorbents (Figure 1). $ZnCl_2$ was used as the activating agent in the reaction. Carbonization occurs at temperatures varying from 300 to 500 degrees Celsius.

The first stage was a thorough cleansing. Corn cobs were thoroughly cleaned with distilled water to remove any remaining debris, dirt, or dust. The maize cob was sun-dried for 48 hours and then heated to 110 degrees Celsius in a hot air furnace for at least 2 hours to eliminate moisture. Once a fresh maize cob was gathered, it was pre-carbonized in the oven for an hour at 400 degrees Celsius to remove the volatile chemicals, as illustrated in Figure 2a. The maize cobs were crushed twice in a grinder after being crumpled into tiny pieces using a mortar. Corn cobs were sieved twice with 0.2, 0.4, and 0.6-millimeter sieves for 30 minutes to achieve a consistent size, as illustrated in Figure 2b.

Figure 1. Raw corn cobs.

a B

Figure 2. Corn cobs after pr-carbonized and grind /sieve.

2.3.The Chemical activation

The next stage in the process was the activation step. It consists of submerging the pre-carbonized sample in a zinc chloride solution. Three different approaches were taken to combine the activating agent and the grain [20].

1. *Mixing-filtration*: A zinc chloride-saturated solution was mixed with dehydrated 40- to 60-mesh cob corn for about an hour. After that, the mixture was filtered, desiccated, and activated.
2. *Solid-solid mixing:* The process involved mixing dried corn cobs with pure $ZnCl_2$, which was then activated.
3. *Impregnation*: The homogeneous slurry of dried corn and a saturated $ZnCl_2$ solution was dehydrated at 110°C overnight.

This research adopted a combination of the first and last activation methods.

The samples were immersed in a saturated solution of zinc chloride for six hours with simple stirring. Following this, the samples were filtered and washed with room-temperature distilled water. The filtration and washing were repeated at 50 degrees Celsius three times to ensure the removal of zinc chloride residues. Then, the samples are filtered and put into the drying oven at 150°C for two hours. Figure 3 illustrates the process of activation.

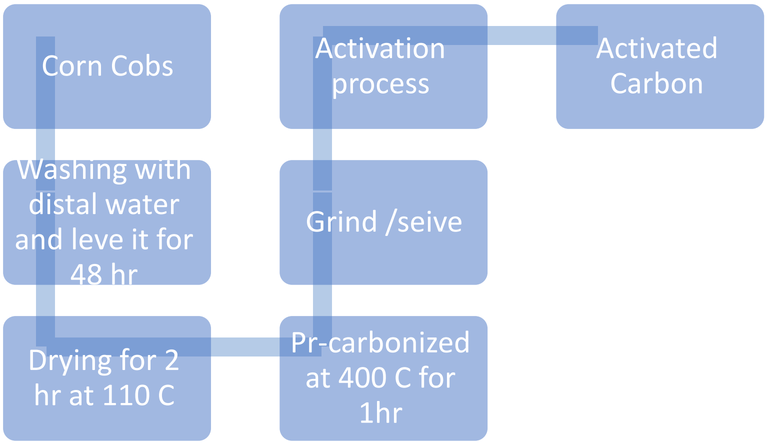

Figure 3. Flow chart of preparation of activated carbon.

2.4. Analyses and characterization

The surface area of every char and the manufactured activated carbons was measured before and after activation utilizing a volumetric adsorption device and the Brunauer Emmett Teller [21](BET) isotherm for nitrogen adsorption at 77 K. BET (Brunauer, Emmett, and Teller) devised and released their theory in 1938. The actual adsorption of gas molecules on a solid surface follows this formula, which is now common knowledge. The BET theory generalized the Langmuir theory's principle of monolayer molecular adsorption to include multilayer adsorption. This theory relies on the following assumptions:

1. Langmuir's theory applies to all layers.
2. None of the adsorption layers interact.
3. Infinite layers of gas molecules physically adsorb on a solid.

To determine micropore volume, de Boer developed the t-plot method for analyzing isotherm data. In a certain isothermal area, it is assumed that all micropores have already been filled. On the other hand, the adsorption in larger pores follows an equation that is typical of a broad category of materials. Adsorption in macropores and mesopores would be approximated by this equation. It is also similar to adsorption on a flat surface at low pressure, where the micropores are not entirely filled, but the mesopores are not yet vapor-saturated.

3. Results and Discussion

3.1. Particle size

Figures 4 and 5 depict the influence of particle size (from 0.2 to 0.8 mm) on the BET surface area and pore size of maize cobs. The carbonization duration, activation temperature, and chemical-to-corn ratio in this sequence of samples were all set to 2 hours at 400 degrees Celsius. Figure 4 shows a slight difference between the surface areas of activated carbon (0.2 and 0.4). However, the surface area of activated carbon with a diameter of 0.4 is greater than 0.2. This higher surface area may be due to the distribution of slightly wider pores (10), while the 0.6 mesh size has a very small surface area. From these results, it can be concluded that the activated carbon surface area increases as its diameter decreases. It can also be shown in Figure 5 that the pore size of activated carbon increases as the surface area decreases.

3.2 Activation agents

Figure 5 shows the surface area value of three samples of activated carbon prepared with different measurements and at a temperature of 400°C, which were activated using zinc chloride. We notice from the figure that the surface area increased by approximately ten times after activation using the activating agent compared to what it was before using the activating agent. The size of activated carbon particles directly impacts the yield and porosity of the resultant carbons, whereby an increase in particle size reduces both. The observed phenomenon could be explained by the notion that larger particles possess a relatively reduced external surface area available for interaction with the chemical reagent, in addition to exhibiting a heightened resistance to intraparticle diffusion of the reagent.[22]

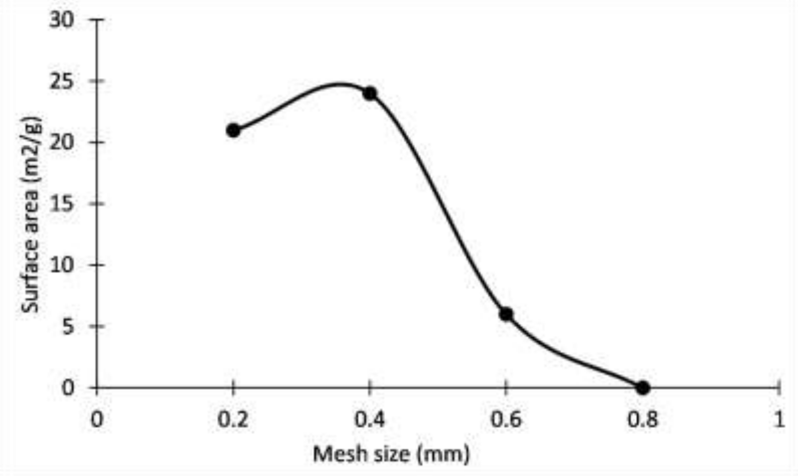

Figure 4. Mesh size impact on the surface area.

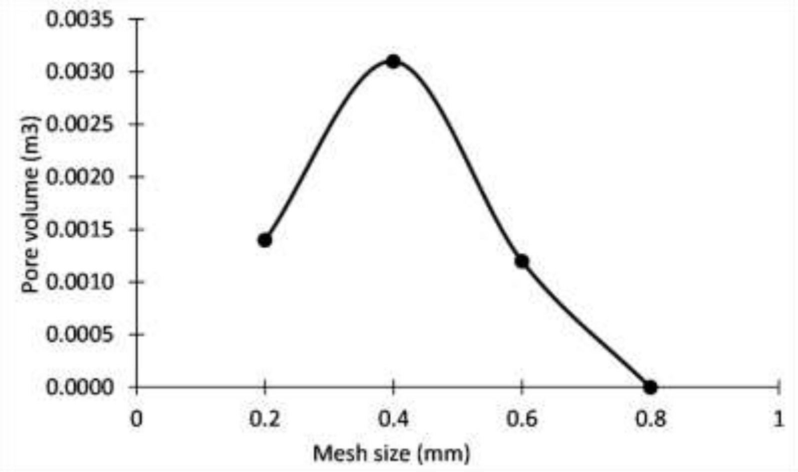

Figure 5. Mesh size impact on pore volume

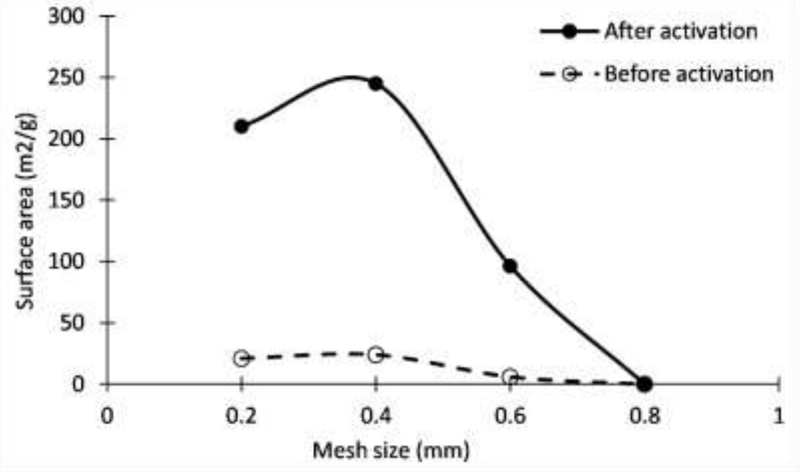

Figure 6. Influence of the activation process on the surface area

4. Conclusions

The generation of porous carbon through the utilization of biomass waste materials is of utmost significance in addressing environmental remediation concerns. The pore structure and characteristics of carbon are closely linked to both the type of biomass and the conditions under which carbonization occurs. The present investigation entailed the production of multiple porous, biomass-derived activated carbon (AC) substances utilizing $ZnCl_2$ as the pore-generating component. A study investigated the influence of the prepared carbon diameter and the activated agent on the resultant carbon's pore size and surface area. The study involved the determination of three carbon diameters, measuring 0.2, 0.4, and 0.6 mm. The study revealed that optimal surface area and pore size were achieved through activation before and after treatment, with a carbon diameter of 0.4 mm and a surface area of 245 m^2/g.

References

1. Zhuo Y Z, Qi Y, Xiao M L, Kun L, Yang L and Guang M Z 2012 Ind. Crops Prod. 37 178 1-
2. Awitdrus, Deraman M, Talib I A, Omar R, Jumali H, Taer E. and Saman M M 2010 Sains Malaysiana 39 83
3. Omri A, Benzina M and Ammar N 2013 Journal of industrial engineering chemistry 19 2092 -4
4. Taer E, Deraman M, Talib I A, Umar A A, Oyama M. and Yunus R M. 2010 Curr. Appl. Phys. 10 1071 -3
5. Elmouwahidi A, Zapata-Benabithe Z, Carrasco-Marin F and Moreno-Castilla C 2012. Bioresour. Technol. 111 185
6. Li W, Li-bo Z, J-Hui P, Ning-Li, Xue-Yun Z 2008 Ind. Crops Prod. 27 341 5-
7. Foo K Y dan Hameed B H 2012 Microporous Mesoporous Mater. 148 191
8. Farma R, Deraman M, Awitdrus A, Talib I A, and Basri N H 2013 Bioresour. Technol. 132 254 7-
9. Farma R, Deraman M, Soltaninejad S, Awitdrus, Taer E, Ishak M M, Nor N S M, Basri N H, Dolah B N M, Othman N K, Othman M A R, Daik R, Suleman M and Hegde G 2015. Electrochemistry 83(12) 1053
10. Awitdrus, Annur A, Farma R, Iwantono and Deraman M 2017 AIP Conference Proceedings 1801 04000211. Liang, H.; Song, B.; Peng, P.; Jiao, G.; Yan, X.; She, D. Preparation of three-dimensional honeycomb carbon materials and their adsorption of Cr (VI). *Chem. Eng. J.* **2019**, *367*, 9–16. [Google Scholar] [CrossRef]
11. Sudha R., Srinivasan K., Premkumar P. Removal of nickel (II) from aqueous solution using Citrus Limettioides peel and seed carbon. *Ecotoxicol. Environ. Saf.* 2015;117:115–123. doi: 10.1016/j.ecoenv.2015.03.025. [PubMed] [CrossRef] [Google Scholar]

12. Jin J., Li S., Peng X., Liu W., Zhang C., Yang Y., Han L., Du Z., Sun K., Wang X. HNO_3 modified biochars for uranium (VI) removal from aqueous solution. *Bioresour. Technol.* 2018;256:247–253. doi: 10.1016/j.biortech.2018.02.022. [PubMed] [CrossRef] [Google Scholar]
13. Block I., Günter C., Rodrigues A.D., Paasch S., Hesemann P., Taubert A. Carbon Adsorbents from Spent Coffee for Removal of Methylene Blue and Methyl Orange from Water. *Materials.* 2021;14:3996. doi: 10.3390/ma14143996. [PMC free article] [PubMed] [CrossRef] [Google Scholar]
14. Campos G.A.F., Perez J.P.H., Block I., Sagu S.T., Celis P.S., Taubert A., Rawel H.M. Preparation of Activated Carbons from Spent Coffee Grounds and Coffee Parchment and Assessment of Their Adsorbent Efficiency. *Materials.* 2021;9:1396. doi: 10.3390/pr9081396. [CrossRef] [Google Scholar]
15. Kamedulski P., Gauden P.A., Lukaszewicz J.P., Ilnicka A. Effective Synthesis of Carbon Hybrid Materials Containing Oligothiophene Dyes. *Materials.* 2019;12:3354. doi: 10.3390/ma12203354. [PMC free article] [PubMed] [CrossRef] [Google Scholar]
16. Li F., Zimmerman A.R., Hu X., Yu Z., Huang J., Gao B. One-pot synthesis and characterization of engineered hydrochar by hydrothermal carbonization of biomass with $ZnCl_2$. *Chemosphere.* 2020;254:126866–126871. doi: 10.1016/j.chemosphere.2020.126866. [PubMed] [CrossRef] [Google Scholar]
17. Ozdemir I., Şahin M., Orhan R., Erdem M. Preparation and characterization of activated carbon from grape stalk by zinc chloride activation. *Fuel Process. Technol.* 2014;125:200–206. doi: 10.1016/j.fuproc.2014.04.002. [CrossRef] [Google Scholar]
18. Nassar H., Zyoud A., El-Hamouz A., Tanbour R., Halayqa N., Hilal HS Aqueous nitrate ion adsorption/desorption by olive solid waste-based carbon activated using $ZnCl_2$. *Sustain. Chem. Pharm.* 2020;18:100335–100343. doi: 10.1016/j.scp.2020.100335. [CrossRef] [Google Scholar]
19. Ahmadpour, A. and Do, D.D., 1997, The preparation of activated carbon from macadamia nutshell by chemical activation. Carbon, 35: 1723.
20. Brunauer, Stephen; Emmett, P. H.; Teller, Edward (1938). "Adsorption of Gases in Multimolecular Layers". Journal of the American Chemical Society. 60 (2): 309–319. Bibcode:1938JAChS..60..309B. doi:10.1021/ja01269a023. ISSN 0002-7863
21. Chen, T.; Gu, W.; Li, G.; Wang, Q.; Liang, P.; Zhang, X.; Huang, X. Significant enhancement in catalytic ozonation efficacy: From granular to super-fine powdered activated carbon. Front. Environ. Sci. Eng. 2017, 12, 6. [Google Scholar] [CrossRef]