



# Proceeding Paper Reduction in Oil and Grease from Degreaser Discharged Tank via Adsorption Process Using Microwave-Carbonized Corn Cobs<sup>+</sup>

Eric L. Hernandez<sup>1</sup>, Allan N. Soriano<sup>2</sup> and Rugi Vicente C. Rubi<sup>3,\*</sup>

- <sup>1</sup> College of Engineering Architecture and Aviation, University of Perpetual Help System, Binan 4024, Philippines; hernandez.eric@uphsl.edu.ph
- <sup>2</sup> Department of Chemical Engineering, Gokongwei College of Engineering, De Lasalle University, Manila 1400, Philippines; allan.soriano@dlsu.edu.ph
- <sup>3</sup> Chemical Engineering Department, College of Engineering, Adamson University, Manila 1400, Philippines
- \* Correspondence: rugi.vicente.rubi@adamson.edu.ph
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**Abstract:** The effects of rapid industrialization created an enormous burden on the environment. The quality of the water source is drastically affected by the discharge coming from industry and domestic usage. Nowadays, the treatment of wastewater involves the use of chemicals, and powder-activated carbon made from agricultural waste is commonly used. This study used corn cob wastes activated with sodium chloride in a 1:2.5 ratio and utilized a microwave. The percent adsorption for powder-activated carbon (PAC) from corn cobs with microwave heating reached 93% removal of oil and grease for a 10 g dosage, while 87% was reached for powder-activated carbon without microwave heating. Freundlich and Langmuir isotherms both represent the behavior of PAC, and the breakthrough time decreased as the flow rate of contaminants increased in the continuous flow system. The characteristics of powder-activated corn cobs contained a lot of grooves, crevices, and cracks, and the macropores deep inside the surface were highly developed, which is typical for an activated carbon that facilitates an effective adsorption process. The pore volume was found to be 1.3 cm<sup>3</sup>/g for PAC with microwave heating and 1.5 cm<sup>3</sup>/g for that without microwave heating. The pore volume determined the adsorption capacity of PAC from corn cobs.

**Keywords:** adsorption; corn cobs; Freundlich and Langmuir isotherms; microwave heating; oil and grease; powder-activated carbon

## 1. Introduction

Setting up wastewater treatment is a common standard part of the operational project of the plants whose line of manufacturing uses water in their industrial processing line. One of the industries that uses water in their process lines is metal fabrication with painting sections. Prior to painting, there is a degreaser tank whose main function is to eliminate oil and grease on the surface of the metal prior to the application of paint. The degreaser contains a lot of contaminants aside from its chemical content, which is mostly surfactant in nature. These contaminants include oil and grease, soluble and non-soluble particles, color, and a high level of chemical and biological oxygen demand, which, when not treated, will affect the quality of the water, like the rivers or lakes that serve as the catch basins for these water pollutants. Chemical treatment is so far one of the most effective ways of treating the degreaser wastewater discharged, and part of that treatment is the carbon adsorption section of the water chemical treatment line.

Many research studies on the use of activated carbon derived from different agricultural waste products have been conducted. In one study, walnut and almond shells were



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). used as raw materials for activated carbon and used to remove the methylene blue dye [1]; rice husks and corn cobs were used to remove the phosphate waste [2], and similarly, maize corn cob activated carbon was used to remove lead contaminants from wastewater [3]. Many studies used corn cobs as a precursor in removing waste like iron and chromium [4] and remazol brilliant blue R dye [5]. Although interest in corn cobs has grown, much more needs to be explored.

Thus, it is the main aim of the present work to determine the adsorption performance of corn cobs. Specifically, this study (i) created a powder-activated carbon from corn cobs via microwave-assisted and non-microwave-assisted (thermal) processes with sodium chloride as the activating agent; (ii) characterized the microwave-assisted and thermally carbonized corn cobs; and (iii) used batch tests and continuous fixed flow to determine the breakthrough time, Freundlich and Langmuir isotherms, and percent adsorption.

## 2. Materials and Methods

## 2.1. Preparation of Corn Cobs

The corn cobs were obtained from the local markets of Biñan and Sta. Rosa Laguna. A total of 10 kg of corn cobs were bought, and the kernels were manually removed. The corn cobs were washed 5 times using distilled water to remove any dirt or impurities. They were dried under the sun for 1 week and powdered using a milling machine. They were then sieved to get the particle size distribution. The moisture content was determined before it was placed in an airtight container.

## 2.2. Carbonization Process

Twelve crucibles were prepared, and 2 g of powdered corn cobs was placed in each crucible. The furnace was set to 4 different temperatures (150, 200, 250, and 300 °C) with 3 different time intervals (1, 2, and 3 h) for each temperature. Each crucible was placed at a specific temperature and time interval. The results were recorded for observation and comparison, and one crucible was chosen based on its appearance, qualitatively. This served as the basis for the best temperature and time for the production of a large amount of carbonized corn cobs. The temperature of 300 °C and the time of 1 h were considered the best conditions to carbonize the corn cobs.

## 2.3. Activation Process

Two 1.5 L beakers were prepared, and 250 g of laboratory-grade NaCl was added to each of the two beakers. Then, 1.2 L of distilled water was added and mixed until the salt was dissolved. An amount of 100 g of carbonized corn was added to each of the salt solutions, slowly stirred for 8 h using the stirring plate, and allowed to stand for 24 h. It was transferred into another beaker, placed on a hot plate, and heated to 120 °C until it became a paste-like form. The contents of the first beaker were placed in 20 porcelain crucibles with covers and placed in a furnace with a temperature set at 300 °C for 1 h. It was allowed to cool and placed inside the filter cloth bin. It was washed by running 18 L of distilled water to ensure that no more salt was coming out of the filter cloth. The ion concentration of the filtrate was checked using a portable conductivity meter, and after it reached a reading of 5 ppm or less, the washing was stopped. The solid particles were removed from the cloth, placed in a pan, and dried in an oven at 105 °C for 12 h. It was placed in a clean, airtight container and labeled with activated carbon without microwave heating.

The contents of the second beaker were placed in a microwaveable pan, placed inside the microwave oven, and set at 500 W for 20 min. They were allowed to cool and placed inside the filter cloth bin. The contents were washed by running 18 L of distilled water to ensure that no more salt was coming out of the filter cloth. The ion concentration of the filtrate was checked using a portable conductivity meter, and after it reached a reading of 5 ppm or less, the washing was stopped. The solid particles were removed from the cloth, placed in a pan, and dried in an oven at 105 °C for 12 h. It was placed in a clean, airtight container and labeled with activated carbon with microwave heating.

## 2.4. Characterization

Ten grams each of carbonized charcoal and activated carbon with microwave heating and without microwave heating were sent to UP Diliman, College of Chemical Engineering and Chemistry, for a Scanning Electron Microscopy analysis to test the surface morphology using 10 microns of magnification. Another 10 g each of activated carbon with microwave heating and without microwave heating were sent to the Department of Science and Technology, Standard and Testing Division, to test the percentages of the carbon, hydrogen, and nitrogen content of the sample using the combustion method.

#### 2.5. Batch Testing

The batch testing was conducted for the purpose of assessing the adsorption performance of the prepared activated carbon from corn cobs. It was also used to obtain the plots to model the appropriate isotherms. The parameter used to test the adsorption performance is the percent adsorption of oil and grease. The first set of samples, using 1, 5, and 10 g of activated carbon with and without microwave heating, was sent to Mach Union Laboratory for oil and grease adsorption testing using the partition gravimetric method. The second set of samples was assessed in Mapua University's Environmental Engineering Laboratory for oil and grease using the isotherm modeling batch test.

#### 2.6. Isotherm Modeling Batch Test

A mixture of oil and water was prepared by adding 1 g of oil to five 500 mL Erlenmeyer flasks. In the first flask, 1 g of activated carbon with microwave heating was added; in the second flask, 2 g was added; in the third flask, 3 g was added; in the fourth flask, 4 g was added; and in the fifth flask, 5 g was added. The flasks were agitated for 5 h using a magnetic stir plate and filtered using a Buchner filter set up. The oil and grease were analyzed using the gravimetric partition method. Equations (1) and (2) were used to calculate the x/m and C<sub>e</sub>. The x is the difference between the initial mass of the oil before adsorption and the final mass of the oil after adsorption in the sample. The m is the mass of the adsorbent used. Ce is the concentration of the oil–water mixture after adsorption. The curve was plotted for the Freundlich and Langmuir isotherms, and the best fit was determined via means of the coefficient of determination.

$$\frac{1}{q_e} = \frac{1}{Q^o} + \frac{1}{KQ^o} \cdot \frac{1}{C_e}$$
(1)

Where:  $q_e$  is the amount of the adsorbate per mass of adsorbent (mg/mg), *K* is the energy of adsorption,  $Q^0$  is the adsorption capacity,  $C_e$  is equilibrium concentration of the adsorbate.

$$\log q_e = \log K_F + \frac{1}{n} \log Ce \tag{2}$$

Where  $\frac{1}{n}$  is the adsorption intensity.

#### 3. Results

#### 3.1. Carbonization Results of Corn Cobs

Based on the different samples prepared for the optimization of the best time and temperature for the carbonization of the precursor corn cobs, the temperatures used were as follows: 150 °C, 200 °C, 250 °C, and 300 °C at different carbonization times of 1, 2, and 3 h per temperature; the optimum time and temperature selected were 1 h and 300 °C. The basis of the selection was the appearance of the carbonized corn cobs, as shown in Figure 1.



Figure 1. Carbonized corn cobs at different pyrolysis temperatures.

#### 3.2. Characterization Results of PAC

Table 1 shows the characteristics of activated carbon from corn cobs used in this paper. It was compared with those found in related research. There was only a slight difference in the values between the PAC with microwave and non-microwave heating in comparison to the data from other research in all aspects of the parameters, which show that the prepared activated carbon from maize corn cobs was expected to perform effectively in terms of contaminant removal in wastewater, specifically oil and grease, via the adsorption process. In some literature, the C content is as high as 78% [2]. Most of the activated carbon derived from agricultural materials has values ranging between 41.23 and 84.50% C, 4.63 and 6.26% H, and 0.7 and 4.10% N [6]. The moisture content was slightly higher as compared to the literature in the table, but in some studies, the percentage of moisture was reported as 15.47% and 13.2% [6], which are double in value in comparison to this paper. The pore volume for PAC corn cobs with and without microwave heating was a little bit higher than was found in the literature, but it was still within the values of the ASTM range of  $0.68-2.80 \text{ cm}^3/\text{g}$ . Microwaves create a direct heating of the particle interior as compared to conventional heating, where the surface of the particle is heated before its interior, inducing a thermal gradient between the surface and the core of each particle. A 500 W power source with an activation time of 20 min was used, and in some literature, the power increased from 550 W to 700 W up to 1000 W. A sign of a decrease in adsorption was noticed at 1000 W because excessive microwave energy could burn the carbon, destroying the pore structure.

Parameters	PAC with Microwave Heating	PAC without Microwave Heating	Literature	Reference
pH	7.7	7.4	6.4	[7]
Density	0.4 g/ml	0.33 g/ml	0.47 g/ml	[7]
% Moisture	7.4	7	5	[7]
Iodine No.	550 mg/g	540 mg/g	453 mg/g	[8]
Surface Area *	900 mg/g	900 mg/g	504 mg/g	[8]
Ash Analysis	3.4%	4%	8.9%	[9]
Pore Volume	1.3	1.5	1.1 cm <sup>3</sup> /g	[2]
% C	64.7	55.5	52.31	[10]
% N	4.55	4.84	3.38	[10]
% H	0.915	1.16	1.02	[10]

 Table 1. Physical characteristics of powder-activated carbon (PAC) from corn cobs.

\* Estimated iodine number.

The SEM result of PAC corn cobs with microwave heating is shown in Figure 2a. It contains a lot of grooves, crevices, and cracks. The macropores deep inside the surface were highly developed. Macropores served as transport channels for the adsorbate into the

micropores and mesopores [7]. The high iodine value of 550 mg/g, which gives an estimate amount of micropores [11], explains the reason for the high adsorption percentage (96%) since 95% of the total surface area is covered by the specific area of micropores [7]. The same analysis is given to PAC corn cobs without microwave heating, as shown in Figure 2b, magnified at 10 microns. Groves, crevices, and cracks are also visible. Macropores are highly developed inside the surface, and the high iodine value of 540 mg/g is due to the macropores branching into mesopores and mesopores branching into micropores [7], giving them a high adsorption capacity (96%).



Figure 2. (a) SEM PAC corn cobs with microwave heating; (b) SEM PAC corn cobs without microwave heating.

## 3.3. Equilibrium Batch Test of Oil and Grease Using In-House Laboratory Testing

The results of the batch test for oil and grease using 500 mg of oil spike in 250 mL water and applying 5 g of PAC corn cobs with and without microwave heating are shown below:

The graph in Figure 3a shows that at a time equal to 15 min, the concentration of oil and grease in the adsorption solution reaches its equilibrium value. The adsorption percentage is 96.3%, and the adsorption capacity is 27.24 mg/g. Figure 3b, on the other hand, reaches equilibrium time after 25 min with adsorption percentage equal to 96% adsorption. Both types of PAC corn cobs exhibit the same amount of adsorption at a 5 g dosage.



**Figure 3.** Concentration versus time graph of batch equilibrium test using PAC corn cobs with (a) and without (b) microwave heating: ♦data from this work.

The high adsorption percentage, which was 96.3% for powder-activated carbon with microwave heating and 96% adsorption for powder-activated carbon without microwave heating, was related to the high carbon content after carbonization.,. The reason for this is that during carbonization, elements such as oxygen, hydrogen, nitrogen, and sulfur are removed as volatile gaseous products. This leaves the residual elementary carbon atoms to

form stacks of aromatic sheets that are a good foundation for the creation of pores, which are enhanced during the activation process.

The low percent ash for powder-activated carbon with microwave heating, which was 3.4% and 4%, in the case of powder-activated carbon without microwave heating, was related also to the high performance of the activated corn cobs since the lower the ash percent, the higher the ability of the carbon to adsorb contaminants since ash constitutes the inorganic part of the carbon [12,13].

In comparison with the performance of activated carbon from corn cobs is comparable with the other methods of removing oil and grease together with the percent removal.

## 3.4. Isotherm Modeling

The model selected in terms of isotherm depends upon the value of the highest R and the n value for Freundlich. The n must be in unity because less than 1 value means there are poor adsorption characteristics. Below is the graph of Langmuir and Freundlich isotherms for PAC corn cobs with and without microwave heating. The graphs show the appropriate isotherm suitable for the PAC used in this paper and the corresponding isotherm equation.

Based on Figure 4a,b and Figure 4c,d and given the value of  $\mathbb{R}^2$ , both isotherms indicate a strong piece of evidence for the adsorption of oil and grease to PAC corn cobs with and without microwave heating. This indicates that the adsorption of oil and grease from the synthetic wastewater could be either monolayer or multilayer. This was the same finding conducted during the adsorption of  $\mathbb{Cr}^{6+}$  using activated rice husk carbon [13,14]. The high adsorption percentage during the preliminary and equilibrium batch tests is primarily due to the high adsorptive capacity of any adsorbent materials [15], which is 1065 mg/mg for PAC with microwave heating and 578.1 mg/mg for PAC without microwave heating.



**Figure 4.** Isotherm model equation. (a) Langmuir Isotherm ( $R^2 = 0.9933$ ). (b) Freundlich Isotherm ( $R^2 = 0.9978$ ). (c) Langmuir Isotherm ( $R^2 = 0.9055$ ). (d) Freundlich Isotherm ( $R^2 = 0.9712$ ) of PAC corn cobs without and with microwave heating, respectively.

#### 4. Conclusions

The study showed that the prepared PAC corn cobs are comparable in terms of those found in the other literature. The SEM analysis reveals the cracks, grooves, and crevices due to the reaction of sodium chloride with carbon, making those sites available for contaminants. The batch test confirmed the effectiveness of the prepared PAC from corn cobs, both using microwave heating and without microwave heating, via adsorbing or removing oil and grease by more than 85% of the initial value. Finally, the Freundlich

isotherms and the Langmuir isotherms are both best suited for PAC corn cobs with and without microwave heating, as  $R^2$  is high for both types of activated carbon.

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