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Carbonization and Chemical Activation Process for the Production of Activated Carbon from Cocoa Shells

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Abstract

Cocoa shells are the waste of cocoa production and correspond to 90% of the fruit, so it is necessary to generate proposals to obtain environmental feasibility for the production of activated carbon. Therefore, the purpose of this study was to develop a proposal for the application of the carbonization and chemical activation process to obtain activated carbon from cocoa shells in the district of Chulucanas, province of Morropón in Peru. The design used was experimental-unifactorial at two levels: Activation temperature: 500 °C and 650 °C; and Granulometry: +18 mesh, +45 mesh and -50 mesh; where: T°A: Activation temperature (°C); and GR: Granulometry (mm). The result obtained in experiment N°3 slightly exceeds the adsorption capacity of commercial carbon. Likewise, it is concluded that obtaining activated carbon from cocoa shells from cocoa production in Chulucanas by applying the carbonization and chemical activation process is economically viable.

Keywords: *Cocoa Husk; Carbonization process; Chemical activation; Activated carbon.*

INTRODUCTION

Latin America is considered the region with the highest production of the "prime" varieties of cocoa at the international level, since it has about 80% of the world's production, in turn, Peru is internationally recognized for being the center of cocoa biodiversity in the world, with 60% of the cocoa varieties, as well as approximately 35% of the world's production of fine and aroma cocoa. according to the International Cocoa Organization (ICCO), as indicated by the Foreign Trade Society of Peru (Comexperú, 2017).

On the other hand, Piura is the only region in Peru that has the variety of white cocoa, with an approximate production of 450 tons per year, in an area of 120 hectares, being the main producing areas: Chulucanas, Palo Blanco, Charanal, Platanal bajo, Morropón, the lower areas of Bigote, Canchaque, Yamango, Santo Domingo, as well as Montero,

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Paimas and even the district of Tambogrande, which export through the COOP companies. NORANDINO, CASA LUKER DEL PERU S.A.C., ARMAJARO, PERU S.A.C., APPROCAP, as reported by the Ministry of Foreign Trade and Tourism (2017).

As can be seen, the growth of cocoa exports at the international, national and local levels is imminent; However, proportionally to this growth, the amount of waste resulting from the production of the cocoa bean also increases. However, the processes for the final disposal of the waste generated by this (cocoa shells) are still deficient and not very innovative. Currently, they are disposed of inadequately and mostly burned to get rid of them, since they do not have an added value or lack a relevant purpose as could be verified by diagnosis in the area. Due to the aforementioned deficiencies, the following questions were raised: How does the application of the carbonization and chemical activation process allow the obtaining of activated carbon from cocoa shells in the district of Chulucanas, province of Morropón?; Is the chemical composition of cocoa shells from the district of Chulucanas, province of Morropón, ideal for obtaining activated carbon?, What are the optimal conditions of activation temperature and granulometry for obtaining activated carbon?How much activated carbon would be obtained from cocoa shells and what is the percentage of use of them? And finally, the question also arose: Which activated carbon obtained has the highest adsorption capacity?

The purpose of this study lies in the elaboration of a proposal for the application of the carbonization and chemical activation process to obtain activated carbon from cocoa shells in the district of Chulucanas, province of Morropón, for which in this manuscript the objectives will be developed to obtain valid data in the construction of the proposal. Therefore, it is determined if the chemical composition of cocoa shells from cocoa production in the district of Chulucanas, province of Morropón, is ideal for obtaining activated carbon. In addition to determining the optimal conditions of activation temperature and granulometry for obtaining activated carbon from cocoa shells. The amount of activated carbon produced and the percentage of utilization of cocoa shells are also determined. And finally, the adsorption capacity of the activated carbons obtained will be determined.

Likewise, the hypotheses to the problems that arose are related to their better reactivity conditions with the carbonized ones, the process of carbonization and chemical activation will allow the obtaining of activated carbon from cocoa shells in the district of Chulucanas, province of Morropón. Also due to the chemical composition of cocoa shells, it is an ideal raw material for obtaining activated carbon; the optimal conditions for obtaining activated carbon by chemical activation would be: 500 °C activation temperature and with a grain size of -50 ASTM; the percentage of use of cocoa shells would be 20% of the raw material used; and activated carbons obtained at 500 °C activation temperature and with a grain size of -50 ASTM, have an excellent adsorption capacity unlike carbons obtained under other operating conditions.

Theoretical basis

The study by Jiménez and Mantilla (2016) on the use of cocoa pod shells in the production of activated carbon for wastewater treatment in Colombia; It shows the use of low-cost raw materials (lignocellulosic waste), from which you can obtain a higher value-added product to reduce water pollution and lower your treatment costs.

Next, Plaza Recobert (2015) evaluates new precursors and the activation process with carbon dioxide in Spain; where he evaluates two new lignocellulosic precursors: cocoa husk and loquat pit, from which activated carbon can be obtained.

Continuing with the study by Luna et al. (2007) on the production of activated carbon from coconut shells in Mexico, they present a proposal for the theoretical design of a pilot unit for obtaining activated carbons from coconut shells.

To reinforce the background of the study, Lozano, Barreto and Sepúlveda (2015), in their

Pre-Feasibility Study for the installation of an industrial plant to obtain activated carbon from sugarcane bagasse (Saccharum Officinarum) in the Loreto-Iquitos Region; It assesses the technical and economic feasibility at the pre-feasibility level for the installation of an industrial activated carbon plant. On the other hand, Carrillo and Lembcke (2015) in another Pre-Feasibility study for the installation of an activated carbon production plant based on coffee husks in Lima, Peru, propose the design of a plant for the production of activated carbon based on coffee husks.

Also in Solé (1989) in his work on a technological study for obtaining activated carbon from steam-activated coconut shells in Lima-Peru, he proposes the method of physical activation as a procedure for obtaining activated carbon from lignocellulosic waste.

Likewise, no previous work has been reported in the Piura region, referring to the obtaining of activated carbon from cocoa shells, using the process of carbonization and chemical activation of the raw material.

The cocoa husk is the waste from cocoa production and corresponds to 90% of the fruit. A percentage of these husks are used as uncomposted fertilizer; however, these are transformed into a culture medium for pathogens that affect the crop significantly. The remaining percentage of the shells are a problem due to their difficulty of storage and lack of application to solve their final disposal (Baena, & García Cardona, 2012, p.19).

Likewise, in October 2018, the Norandino Cooperative reported that in addition to its coffee and panela processing plants, it will have a chocolate plant in the short term, which will process 500 kg of cocoa/h, which means approximately 4000 TN/year, as reported on the page of Agencia Agraria de Noticias (2018). Therefore, the amount of cocoa husks available to obtain activated charcoal is currently higher.

MATERIALS AND METHODS

An experimental study was carried out since the independent variable "carbonization process and chemical activation" were intentionally manipulated to analyze the consequences that this manipulation has on the dependent variable "activated carbon" (Hernández, Fernández & Baptista, 2006). The design used was experimental-unifactorial at two levels: Activation temperature: 500 °C and 650 °C; and Granulometry: +18 mesh, +45 mesh and -50 mesh.; Where: T°A: Activation temperature (°C); and GR: Particle size (mm).

By combining the two levels (T°A and GR), we have: 2 x 3 = 6 sample units. These units had 2 replicates or also called replicates (R), so the sample size (N) was calculated using the following formula:

N = R x T°A x GR, N = 2 x 2 x 3 = 12.

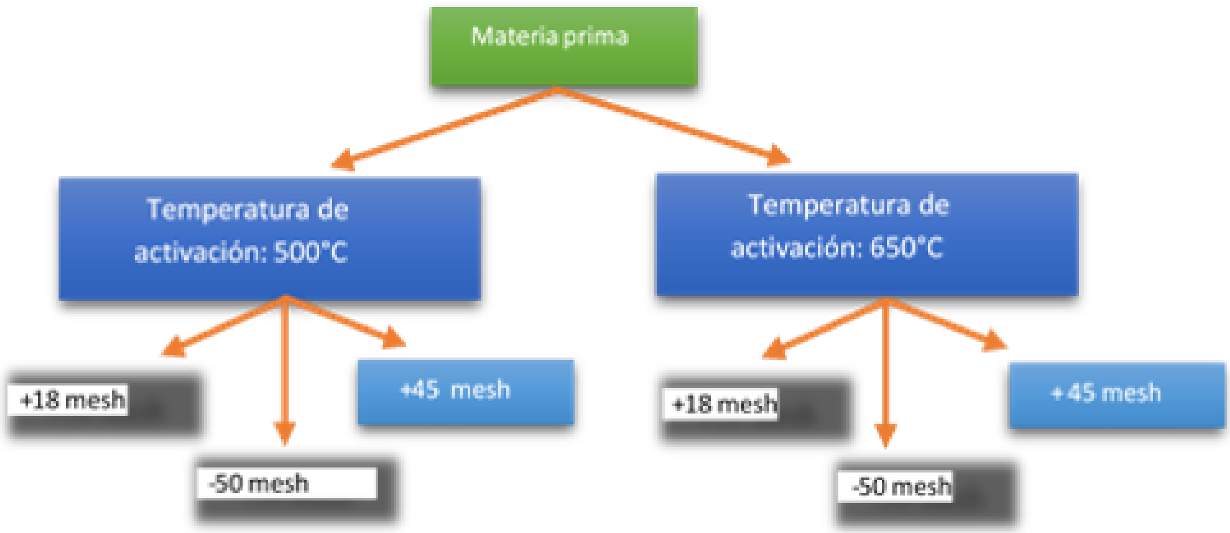

Figure 1. Research design.

Likewise, the research was applied or also called active or dynamic and is closely linked to basic research, since it depends on its discoveries and theoretical contributions. This form of research is aimed at immediate use and not at the development of theories (Rodríguez, 2015).

The study had a descriptive scope, because it allowed the problem to be described and its characteristics to be pointed out in order to submit it to the analysis. The study was cross-sectional according to its temporality. Table 1 shows the data collection.

Table 1. Data collection.

Activation Temperature	Particle size	Data collection
500 °C (T°A1)	+18 mesh (GR1)	T°A1. GR1
	+45 mesh (GR2)	T°A1. GR2
	-50 mesh (GR3)	T°A1. GR3
650 °C (T°A2)	+18 mesh (GR1)	T°A2. GR1
	+45 mesh (GR2)	T°A2. GR2
	-50 mesh (GR3)	T°A2. GR3

For the operationalization of the variables, the main processes for the transformation of a raw material into activated carbon were considered, which were carbonization and activation, either carried out by the physical or chemical method, this process can be carried out under different operating conditions, in this research these conditions were manipulated to obtain activated carbon; Therefore, the process of carbonization and chemical activation is the independent variable of this research.

Likewise, depending on the operating conditions at which it is worked, activated carbons of different characteristics will be obtained, so the activated carbon obtained was the dependent variable of the study.

The population consisted of 20 kg of cocoa husks from cocoa production in the producing areas of the district of Chulucanas, province of Morropón. The sample that was analyzed was 1000 grams, extracted from the 20 kilograms of the population, which were worked at the laboratory level.

The technique used was the observation of the results obtained in the tests carried out at the laboratory level. In addition, direct observation guides were used to collect the data obtained. Both the validity and reliability of the data collection instruments were carried out through the judgment issued by experts; To this end, the revision of the observation guides was requested by three Industrial Engineering specialists from the César Vallejo University in the city of Piura.

Procedure

The process analysis diagrams (DAP) and process operations (DOP), the data obtained were processed using electronic means, classified and systematized through the Excel 2016 package, which allowed the results to be presented through tables and graphs for analysis and interpretation.

Ethical aspects

The authors of the article are responsible for the authenticity of the results obtained, as well as for the reliability of the data provided. His prosecution was truthful and impartial. Likewise, the conditions, regulations and policies of the César Vallejo University were respected, as well as intellectual property, citing at all times the concepts and procedures extracted from previous research and work

RESULTS AND DISCUSSION

To determine that the cocoa husk (raw material used) is ideal to obtain activated carbon, it is necessary to specify the amount of fixed carbon contained in the sample, for this the analysis of 500 grams of cocoa shells was carried out, using the gravimetric method in the laboratory SERVICIOS DE ANÁLISIS Y ASESORÍA DELTAS S.R.L. of the city of Trujillo. department of La Libertad; obtaining the results highlighted in Table 2.

Table 2. Percentage of fixed charcoal in cocoa shells.

Sample	Method	Fixed Carbon
Cocoa Shell	Gravimetric-Ash	48.5%±1.2% (w/w)

Source: SERVICIOS DE ANÁLISIS Y ASESORÍA DELTAS S.R.L.

Likewise, in order to determine the optimal conditions of granulometry and activation temperature, it was necessary to carry out various tests of the carbonization and chemical activation process, for this, a series of procedures were followed in the laboratories of: unitary processes, physical-chemistry and organic chemistry of the School of Chemical Engineering of the Faculty of Mining Engineering of the National University of Piura (UNP). which are detailed below:

- Raw material grinding: To reduce the size of the cocoa shells, an electric mill was used, through which the raw material was passed repeatedly, in order to standardize the size of the waste.

- Sieving of raw material: The ground material was passed through a series of sieves, in order to separate the material by granulometry, using ASTM sieves: 8 mesh (2.38 mm), 12 mesh (1.68 mm), 18 mesh (1.00 mm), 45 mesh (0.354 mm) and 50 mesh (0.297 mm).

- Impregnation of raw material: The cocoa shells were impregnated with phosphoric acid (H3PO4) of 25% concentration, in a ratio of 1/0.5 until a paste-like mixture was obtained. The procedure lasted approximately 04 hours and 06 samples were impregnated: +18 mesh (500°C), +18 mesh (650°C), +45 mesh (500°C), +45 mesh (650°C), -50 mesh (500°C), -50 mesh (650°C).

- Carbonization and Activation of raw material: The samples obtained were entered into the muffle furnace to perform carbonization and chemical activation at two different temperatures: 500°C and 650°C.

- Activated carbon washing: Finally, the activated carbon was subjected to a washing process with hot water at 80°C, to remove any remaining of the activating chemical agent. First, an equal or greater amount of distilled water was added and then the mixture was passed through a filter, to ensure that no traces of the phosphoric acid used for activation remain.

After carbonization and chemical activation of cocoa shells (raw material) in the laboratory, the amounts of activated carbon shown in Table 3 were obtained.

Table 3. Weights obtained from activated carbon.

N° Experiment	Description	Sample Weight (g)	Coal Weight On (g)
01	+18 mesh (500°C)	1.0121	0.2308
02	+18 mesh (650°C)	1.0196	0.1507
03	+45 mesh (500°C)	1.0315	0.2548
04	+45 mesh (650°C)	1.0463	0.2127
05	-50 mesh (500°C)	1.0141	0.1217
06	-50 mesh (650°C)	1.0083	0.0939

To determine the % of yield or % of utilization, the following formula was used, which was worked using Excel spreadsheets (Table 4). charcoal

$$\% \text{ Yield} = \frac{\text{Weight of Activated Carbon}}{\text{Sample Weight}} \times 100$$

Table 4. Determination % utilization or % yield of cocoa shells.

N° Experience	Description	Empty crucible weight (g)	Sample Weight (g)	Total Weight (g)	Crucible Weight + dry sample (g)	Weight of Activated Carbon (g)	% Utilization or % Performance
01	+18 mesh (500°C)	20.1135	1.0121	21.1256	20.3443	0.2308	22.80
02	+18 mesh (650°C)	19.7821	1.0196	20.8017	19.9328	0.1507	14.78
03	+45 mesh (500°C)	19.7887	1.0315	20.8202	20.0435	0.2548	24.70
04	+45 mesh (650°C)	19.7510	1.0463	20.7973	19.9637	0.2127	20.33

N° Experience	Description	Empty crucible weight (g)	Sample Weight (g)	Total Weight (g)	Crucible Weight + dry sample (g)	Weight of Activated Carbon (g)	% Utilization or % Performance
05	-50 mesh (500°C)	23.2728	1.0141	24.2869	23.3945	0.1217	12.00
06	-50 mesh (650°C)	20.2749	1.0083	21.2832	20.3688	0.0939	9.31

Likewise, through the methylene blue test, it was possible to determine the adsorption capacity of each of the activated carbons obtained, this test consisted of adding milliliters (mL) of a solution of methylene blue, which was filtered through 0.1 gram of activated carbon, until saturated. Specifications of quality and reactivation of activated carbon, (Unison Digital Library, Chapter II. 2006, taken from Alarcón, 1971) obtaining the results highlighted in Table 5.

Table 5. Average methylene blue index results.

N° Experiment	Description	Blue Index Methylene (mL/0.1g)
-	Commercial Coal	12
01	+18 mesh (500°C)	10
02	+18 mesh (650°C)	7
03	+45 mesh (500°C)	14
04	+45 mesh (650°C)	9
05	-50 mesh (500°C)	6
06	-50 mesh (650°C)	5

Likewise, the economic viability for the production of 01 kg of activated carbon from cocoa shells was evaluated in a quick and simplified way, according to the experimentally obtained data, which are highlighted in Table 6.

Table 6. Production costs of 01 kg of activated carbon from cocoa shells.

Parameters	Production Costs
Raw material	S/. 0.00
Raw Material Transportation Costs	S/. 20.00
Raw material treatment - 01 kg. (Includes use of equipment in the laboratory)	S/. 20.00
Conversion of raw material to activated carbon - 01 kg. (Includes chemical reagents and use of laboratory equipment)	S/. 100.00
TOTAL	S/. 140.00

Activated Carbon Value (01 kg).	S/. 170.00

As can be seen, obtaining activated carbon from cocoa husks is economically viable, so it is proposed to design the capacity of an industrial plant for its production.

Discussion

Fixed carbon is usually considered to be the main component of coal, the theory indicates that it corresponds to pure carbon. For this reason, the average fixed carbon values can vary from 40 to 80% for obtaining charcoal, but Gonzáles and Teruya (2014) mention that, for a charcoal to have good adsorption characteristics (activated carbon), the values must exceed 45%. Thus indicating fixed carbon values so that they are directly related to the quality of the coal, which in turn depends on the treatment temperature (Gonzales and Teruya, op. cit.)

Therefore, from the result shown in Table 5, it is shown that the raw material used (cocoa shells) is ideal for obtaining activated carbon, since almost 50% of its chemical composition is fixed carbon.

According to laboratory results and technical standards for activated carbon: NTP 207.024:1982 and NTP 311.331:1998; It is verified that the optimal conditions of activation temperature and granulometry are those worked in experiment N°3: granulometry +45 mesh and 500°C (INCP-Instituto Nacional de Calidad Peruana (1998).

As can be seen in Table 6, a greater amount of activated carbon (0.2548 grams) was obtained with experiment N°3, corresponding to the process carried out with +45 mesh granulometry and 500°C activation temperature. Likewise, it can be seen that the lowest amount of activated carbon (0.0939 grams) was obtained with experiment N°6, corresponding to the process carried out with -50 mesh granulometry and 650°C activation temperature.

The results obtained agree with the theories of Melo (1985) where it is stated that the granulometry and the activation temperature have a significant influence on the quantity and quality of the activated carbon obtained. Likewise, in this study it could be seen that the highest percentage of utilization was 24.70% which was obtained from experiment N°3, corresponding to cocoa shells with +45 mesh of granulometry, which were subjected to the process of carbonization and chemical activation at 500°C.

On the other hand, the lowest percentage of utilization was 9.31% which was obtained from experiment No. 6, corresponding to cocoa shells with -50 mesh granulometry, which were subjected to the carbonization and chemical activation process at 650°C. The result obtained in experiment N°3 is within the average average, compared to the results obtained in previous existing studies.

As can be seen, the highest adsorption capacity was 14 mL of methylene blue/0.1 gram of activated carbon, corresponding to experiment N°3, which was carried out under the following operating conditions: +45 mesh of granulometry and 500°C during the carbonization and chemical activation process.

Likewise, the lowest adsorption capacity was 5 mL of methylene blue/0.1 gram of activated carbon, corresponding to experiment No. 06, which was carried out under the following operating conditions: -50 mesh granulometry and 650°C during the carbonization and chemical activation process.

The result obtained in experiment No. 3 slightly exceeds the adsorption capacity of commercial carbon, according to Specifications for the quality and reactivation of activated carbon, Unison Digital Library, Chapter II. 2006, taken from Alarcón, 1971).

The production cost of 01 kg of activated carbon from cocoa shells is slightly less than the value of 01 kg of activated carbon in the domestic market; However, on a large scale, these costs could be markedly reduced.

CONCLUSIONS

In this study, it was determined that the chemical composition of cocoa shells from cocoa production in the district of Chulucanas, province of Morropón, is ideal for obtaining activated carbon; which contains almost 50% fixed carbon in its composition. In addition, it was determined that the optimal granulometry and activation temperature conditions to obtain activated carbon from cocoa husks are +45 mesh and 500°C respectively. Next, it was determined that the amount of activated carbon obtained was 0.2548 grams with a percentage of use of cocoa shells of 24.70%; and it was determined that the highest adsorption capacity was 14 mL blue methylene/0.1 g of activated carbon, which corresponds to activated carbon obtained under 500°C of activation temperature and +45 mesh of granulometry. Therefore, it is concluded that the activated carbon obtained is of very good quality.

Likewise, it is concluded that obtaining activated carbon from cocoa shells from cocoa production in the province of Morropón, district of Chulucanas, applying the process of carbonization and chemical activation, is economically viable.

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