Revista Mexicana de Ingeniería Química

# OVERVIEW OF THE EFFECT OF ACTIVATING AGENT IN MAXIMUM ADSORPTION AND YIELD OF GRANULAR ACTIVATED CARBON PRODUCTION FROM AGRO-INDUSTRIAL WASTE

G.A. Villalobos-Tudares[1], E. Moreno Rodríguez[2]
*[1]Universidad de las Américas Puebla. gabriel.villalobosts@udlap.mx*
*[2]Universidad de las Américas Puebla. ernestina.moreno@udlap.mx*

Sent date: Day/Month/Year

**Abstract**:

Activated caron (AC) is commonly produced with different agro-industrial residues, which usually do not present an alternative function. To generate the AC, the main step is the activation of the material, which is generally done by chemicals and in some cases using a physical step to increase its properties. A principal component analysis determined that the corn, grape stalks, and sugar cane have a better production relationship with the countries analyzed in a crop investigation with FAOSTAT data. The study collected different investigations in which various materials were activated by diverse agents, comparing the main characteristics of each one. The phosphoric acid dominated the yield comparison with values over the common range, obtaining 70.5% with pecan nutshell and 52.3% with walnut shell. The surface area study determined that potassium hydroxide is the best to improve this variable as it produced a 2202 $m^2/g$ with the sugar cane as raw material, in second place the phosphoric acid presented acceptable results. The adsorption capacity determined that the potassium hydroxide overcomes the phosphoric acid, even though this last one can generate adequate and constant results in this last quality, concluding that these two chemicals overcome as the best activators for AC production.

*Keywords*: activator agent, adsorption, surface area, principal component analysis.

**Resumen**:

El carbón activado (AC) es producido comúnmente con diferentes residuos agroindustriales, los cuales no suelen tener una función secundaria. Para generar el AC, el principal paso es la activación del material, lo cual se hace generalmente con químicos y en algunos casos con pasos físicos para incrementar sus propiedades. EL análisis de componentes principales determinó que el maíz, tallos de uva y caña de azúcar tienen mejor relación de producción con los países analizados en una investigación con datos de FAOSTAT. El estudio recabó investigaciones en las cuales diferentes materiales fueron activados con varios agentes activantes, comparando las principales características de cada uno. El ácido fosfórico dominó la comparación de rendimiento con valores por encima del rango común, obteniendo 70.5% con la cáscara de nuez de pecan y 52.3% con cáscara de nuez. El estudio de área superficial determinó que el hidróxido de potasio es mejor para incrementar esta variable, pues produjo un 2202 $m^2/g$ con la caña de azúcar, seguido por el ácido fosfórico presentando resultados aceptables. La capacidad de adsorción determinó que el hidróxido de potasio superó al ácido fosfórico, aunque este último genera valores constantes y adecuado en esta característica, concluyendo que estas dos últimas sustancias son los mejores activantes en la producción de AC.

*Palabras clave*: agente activante, adsorción, área superficial, análisis de componentes principales.

# 1. Introduction

Activated Carbon (AC) is a term used to define amorphous carbonaceous materials, with properties related to coal or graphite, which also presents a large amount of porosity and an important interparticle surface area. The main characteristic of this material is the huge internal surface area and the number of small pores, both present in its surface, that allows the AC to be used as an adsorbent, retaining molecules that take part in a liquid or gas [1].

The initial matter characteristics and properties determine the treatment that needs to be used in order to generate the desired AC. Among the main raw materials to obtain AC, stand out the by-products of agriculture processes, which means reducing the waste production and adding more yield to the general process. Between these raw materials, the commonly studied are coconut shell [1], [2], palm saw-dust[3], [4], walnut shells [5], [6], sugar canes [7], [8], wood[9], [10], sunflower seeds[11], [12]; all being processed in order to produce several types of AC. Additionally, the application of this type of by-products mentioned before as raw material, generates the advantage of replacing the mineral carbon in the production process of AC, being this one the basic component commonly used before.

The production of AC starts with the preparation of the raw material, that consists of removing all remaining waste, which is important to eliminate any possible organic part of the initial material. The following step is the carbonization of the main substance, which is done at temperatures below 800 °C. The pyrolysis step helps to eliminate elements like oxygen, hydrogen, nitrogen, and sulfur as volatile products. Thus, all materials can be used if they are processed into carbonaceous material, although the properties of the final AC depend on the nature of the activating agent, as well as the conditions used during the activation process [13].

In addition to the production process, it is important to determine the agro-industrial waste materials that can be generated in bigger proportions, so a Principal Component Analysis (PCA) was done in order to establish the relationship between the crop production and the countries around the world. This type of analysis helps study a data set that includes a lot of information, extracting valuable information from the main data and presenting the results as a set of variables called, as its name says, principal components. This analysis also determined out the main countries that can develop a granular activated carbon (GAC)production process due to their massive production of some materials [44].

The objective of this paper is to give a review of the studies using GAC and activating agents at maximum adsorption capacity for the final product. Additionally, a relationship between the activating agents and yield will be stablish, identifying the relation between the final amount of AC generated and the raw material mass. The materials selected for this article were determined by the PCA and the main investigations.

# 2. Environmental context

The United Nations (UN) has set seventeen goals to help achieve sustainable development all around the globe and among those there is the need to ensure sustainable consumption and production patterns. In order to fulfill this topic, the UN determined that is important to generate an efficient use of natural resources and halve the global food waste by 2030, which inevitably includes the agricultural production waste that is generated in the world, because the world total can achieve a total of 4 billion tons in 2050 [14]. Based on previous statement, it is important to consider the role that plays the agroindustry wastes into achieving this goal.

For example, Mexico is considered an agricultural country as it is one of the main activities that take part in the economic development. Among the years, this sector has increased its production reaching more than 231,831,259.55 tons in 2019, considering all agricultural products, according to SIAP (2020) [15]. However, this generates a big problem inside the country, as lot of waste is generated that is not usually treated in the right way or recycled.

In 2017, according to SEMARNAT, Mexico produced 102,895 tons of waste daily. From this number of residues, 83.93% is collected and only 9.63% is recycled, generating an important problem that affects not only the environment, but also avoiding the right use of all available agricultural waste material [16]. Additionally, the National Atlas of Biomass reports an annual residual production of 52,104 tons from agricultural activities, which represents an energetic potential of 796.2 TJ [17].

In table 1, the total production from China, United States, India, Malaysia, Brazil, and Mexico are presented some potential agricultural products or by products that can be used to generate AC. These countries were selected because agriculture represents an important part in their economy scheme, as well as the relevant amount of research they have produced over the last years in the generation of AC studies, helping to improve the development of this topic in their scientific groups [18].

Table 1. Agriculture production per country obtained from FAOSTAT in 2018.

| | Production (tons/year) | | | | |
|---|---|---|---|---|---|
| Country | Coconut | Corn | Sugar cane | Sunflower seed | Walnuts |
| China | 402,684 | 257,348,659 | 108,718,971 | 2,550,000 | 1,586,367 |
| USA | - | 392,450,840 | 31,335,984 | 959,990 | 613,260 |
| India | 11,706,343 | 27,820,000 | 376,900,000 | 200,000 | 32,500 |
| Malaysia | 519,153 | 76,362 | 29,433 | - | - |
| Brazil | 2,346,750 | 82,288,298 | 746,828,157 | 135,872 | 7,373 |
| Mexico | 1,158,471 | 27,169,977 | 56,841,523 | 9,751 | 159,535 |
| World | 61,865,423 | 1,147,621,938 | 1,907,024,730 | 51,954,777 | 3,662,507 |

*2.1. Advantage of using biomass waste.*

The European Union (EU) has been taking in consideration the potential of biomass over the last years, generating different projects in order to use this material to produce a successful impact in its various countries. Most of the ideas are related to energy generation like biogas, liquid biofuels, heating, and electricity, among others, but proving the potential of all the waste that is being produced in the EU. It is reported that between 2010 and 2016, 0.89

million tons of biomass were mobilized as the result of this type of projects, including forest wood, agricultural residues, municipal waste, and food processing residues [19].

The use of biomass waste to produce AC is an important topic to investigate due to the many advantages it involves as it can be the revalorization of the waste, which means that some remnants that are considered waste can be used to produce useful products, generating a progress in treating the huge problem of residue. Most of these agricultural by-products can be used as raw material to generate AC, but it is important to know the production process and how to select it [20]. Another advantage is that synthesized activated carbon are produced from a lower cost process, as the precursor or considered raw material is a renewable source. Additionally, the combustion of these type of AC does not generate an increase in $CO_2$ accumulation as it has been previously captured during the growth of the plant [21], [22]. These benefits play an important part at the moment of taking agricultural waste as a raw material for GAC production.

*2.2. Global development of AC*

It is important to point out that the study of AC production from agro-industrial waste has been increasing over the years, as it has become a suitable alternative to generate this material in order to apply it for wastewater treatment, as well as the many uses mentioned before. Using Scopus data base, the figure 1 was generated, where it can be seen a sample of the number of documents generated for each year from 2009 to 2019. This graph shows that investigations related with AC production from agricultural waste had increased during years all around the world, showing an important advance in the development of this topic [23].

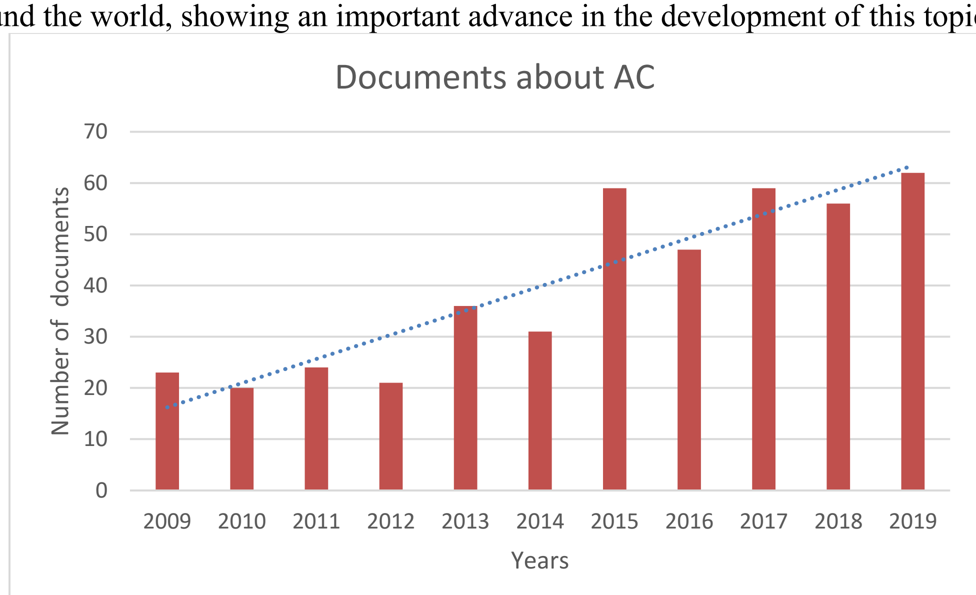


Figure 1. Documents of AC production from agro-industrial waste [23].

In table 2 shows the number of documents related to production of activated carbon from different agricultural products divided by the main countries, which was generated by searching topics about production of activated carbon from agricultural waste. As it can be seen, China is the leading country according to Scopus, as it has generated 600 investigation documents, while the United States has developed 252, and India 244, just for mention some examples. This is important to point out because these countries are also leaders in agricultural production, which means they are trying to find a use to the waste this activity generates [18]. At the same time, this table represents the development in production of AC by country, showing the importance of doing diverse research as it has an important field and different variables to understand its behavior [23].

Table 2. AC´s investigations done by country per agricultural product [23].

| Country | Coconut | Corn | Sugar cane | Sunflower seed | Walnuts | Total |
|---|---|---|---|---|---|---|
| China | 296 | 167 | 27 | 21 | 89 | 600 |
| USA | 105 | 101 | 17 | 10 | 19 | 252 |
| India | 173 | 20 | 36 | 5 | 10 | 244 |
| Malaysia | 114 | 9 | 14 | - | 5 | 142 |
| Japan | 87 | 14 | - | - | - | 101 |
| Brazil | 41 | - | 31 | 4 | - | 76 |

Another important topic to take in consideration, is the flow of activated carbon around the globe, and one good example is that Mexico has increased the production of AC during the past years, since 2003 to 2011 the amount of AC generated raised from 3,108 to 6,581 tons. Nevertheless, the importation grew even more in the same period, going from 4,270 to 8,486 tons each corresponding year. The rising number of imports regarding to exports demonstrate the significant part of this product in the market nowadays, and it is important to decrease the exportation numbers, leading to generate new alternatives to cover the national demand on AC. In Mexico, the companies that dedicate to supply AC are commonly foreigners, but there are few national corporations that produce this material, as Appeals Carbones®, Carboshell ® and Clarimex ® [24] .

*2.3. Use of AC obtained by biomass*

AC is a product often used in the industry due to its properties, adding improvement in the processes that it is applied on, between those functions stand out: recovering precious metals, catalyst for mercury chloride, as a component in ventilation filters and in electrochemical storage for supercapacitors [25]. Nevertheless, one of the main applications of AC is to deodorize and discolor fluids, especially water, because of its high crystallization and porosity, which can be modified and manipulated during its production [26]–[28].

Today, the treatment of wastewater has become an important study for science because it solves some of the main environmental problems that population is facing: reduce contamination in water bodies and producing drinking water for human consumption. The use of this type of carbon is already a relevant part of the solution. Boehler et al. (2012) used AC to remove micropollutants in a municipal wastewater treatment at Switzerland, obtaining an efficiency of 80% while using 10 mg/L and up to 100% for 15 mg/L; adding that the AC can be involved in the biology process as an extra step of wastewater treatment, but a dose of 30 mg/L is needed in order to achieve the 100% efficiency [29],[25]. But as the applications raise, the normal concern with this material is to increase its production.

# 3. Characteristics of AC

The main properties of AC change due to the production process, which involves many variables that are needed to take in account. Over the last years the importance of AC has increased, and the study of its production methodology represents a huge area for research

[30]. One good example is the investigation developed by Lua, Lau & Guo (2006), where they studied the influence of pyrolysis conditions in the pore generation of activated carbon from oil palm shell, variating the temperature, holding time, nitrogen flow and heating rate in the pyrolysis step [31]. As well, Sun & Webley (2010) developed an investigation of the preparation of activated carbon from corncob using different chemical activators: KOH, $K_2CO_3$, NaOH, $ZnCl_2$ and $H_3PO_4$, reporting the comparison between pore volume, external surface, average pore width, among other properties [32].

It is important to point out that there are two types of AC: powdered and granular. The main difference between this classification is the particle size, where the first type is smaller, with the granular activated carbon (GAC) having a greater surface area. Both types can remove taste and odor compounds, which is why they are often used in wastewater treatments in filtration systems. Powdered Activated Carbon (PAC) is commonly applied for gases while GAC is usually for liquids. Nevertheless, a principal factor in choosing each type of AC, is that PAC has higher operational cost and cannot be regenerated, meanwhile GAC is more economic and can be controlled to manage its adsorption and desorption [33].

As mentioned before the superficial area refers to the distance or area of the surface pores that develops in the AC. This property allows to determine the carbon activation level, because the larger the amount of area, the number of zones where adsorption can happen increases in a proportional way, leading to a greater efficiency from the AC while it is accomplishing its function in a wastewater treatment process [30]. According to the International Union of Pure and Applied Chemistry (IUPAC), the pores of an AC can be classified in three main groups according to their dimensions. The first category stands for micropores, having a size inferior to 2 nm and being able to contain molecules that generate odor and taste. Mesopores are categorized between 2 and 50 nm, followed by macropores, which dimensions are greater than 50 nm [34]. All the properties mentioned are defined by the AC production process.

### *3.1. Activation process*

It is important to point out the several types of activations that can be used to produce AC. The first is physical activation, which consists in a heat treatment in a stream of gases, which is commonly done by carbonizing the carbonaceous material in an inert atmosphere, usually done by nitrogen and at a temperature range from 400 to 800ºC, to generate the charcoal [30]. Marsh and Rodríguez-Reinoso (2006) explained that the bonds in the material structure are broken and followed by the second step, which is denominated activation and developed at temperatures from 600°C to 1000ºC, where gas agents work as extractants of carbon atoms, leading to the creation of micropores and the widening of the existing micropores in some cases, leading to the generating of meso and macropores [35].

On the other hand, the process can be developed by chemical activation, where the impregnation step is done by mixing the agent in water and normally done at 85ºC, avoiding the evaporation of the mixture, letting the chemical reactant to swell in the interior of the material structure. After this, the carbonization of the material is done with a flow of an inert gas, followed by a washing process in order to delete any chemical remainders [35].

The activating agent can be an acid or basic substance, but it has been pointed out that acid solutions generate a better quality in the AC, because this type of agent provides ions in the surface, which play an important part on adsorption. Additionally, it is known that some acids are known to produce better results in the AC, as phosphoric acid, due to a structure change in the raw material, generating a division in the bonds and producing resistance in polymers. As well, potassium salts can produce high superficial areas and abundant porosity but require a higher amount of water to eliminate the remaining agent in the final product [36].

The figure 2 shows the process that is commonly used to form AC from any agricultural waste in a laboratory, the activating method is chemical impregnation, which has been described before. The figure shows a more complete methodology with some values assigned to each variable that can be studied from AC production, like carbonization time or temperature, drying periods, heating ramps, among others.

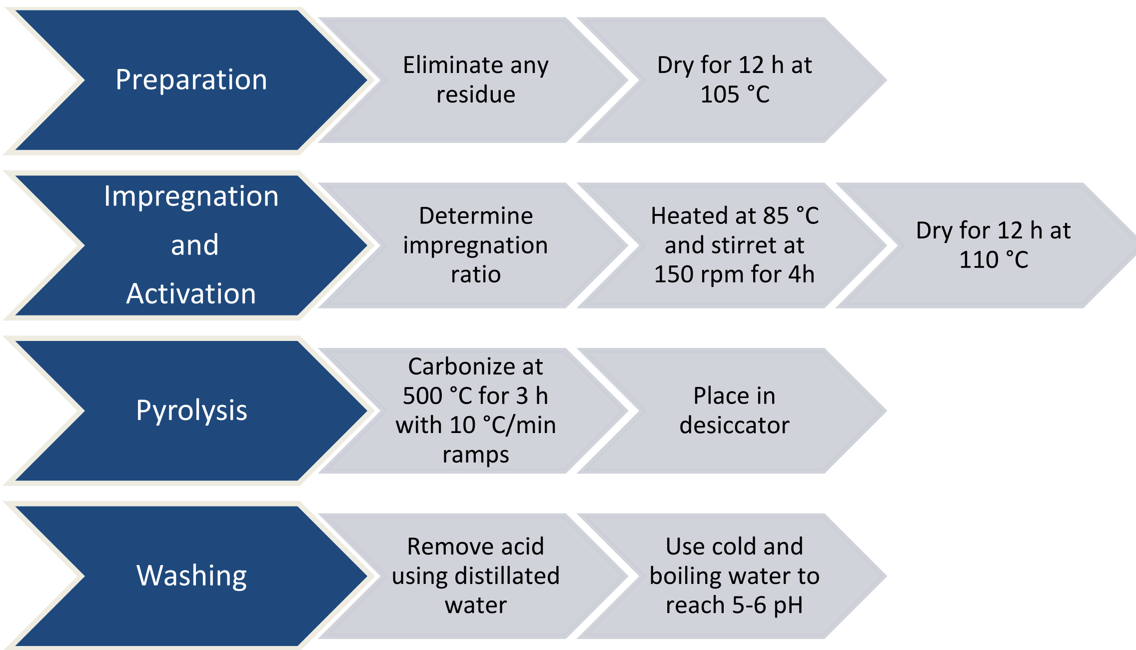


Figure 2. Laboratory process for chemical AC production[36]

*3.2 Characterization*

AC is a complex material that involves a lot of properties, and also, it is a challenge to perform a complete characterization, because there are a lot of techniques of adsorption, kinetics, surface polarities, energetics, among other tests that provide a full characterization [37] . But one of the main properties that are studied is the porosity, which represents the dimensions of the pores in the AC surface and is usually done by scanning with microscopes and small angle scattering of X-rays, the Scanning Electron Microscopy (SEM) is used as qualitative measure while Brunauer-Emmet-Teller (BET) is a quantitative analysis [35].

It is important to mention that not all the AC´s porosity has the same dimensions and can be described by open or closed porosity. The first one applies when the adsorption prefers smaller size molecules instead of larger size, and the second one when is closed to molecules of bigger size than small ones, closed porosity is also defined when it is not accessible to a certain adsorbate [35].Even though the porosity is important, the main test used for characterization of activated carbon is adsorption isotherm. Once it is known, the adsorption process is possible thanks to Van der Waals forces and chemical bonds, an adsorption isotherm is the relation between the mass of an adsorbed solute and the concentration of solute once the equilibrium is achieved [38].

Langmuir and Freundlich´s models are the most common ones used to describe the adsorption isotherm observations. The first model (Eq. 1) describes adsorption as single layered where the regions on the surface of the adsorbent material are uniform; while Freundlich (Eq. 2) defines the process if the adsorption happens in mono layer but not uniform nor homogenous. By properly using these models, the main properties of an adsorption system can be defined, such as the concentration of the adsorbate in the fluid ($C_e$), which determines the equilibrium point, the maximum capacity of adsorption by unit of adsorbent ($Q_0$) and the amount of solute adsorbed ($q_e$). According to Faust (1983) the Freundlich and Langmuir constants, $K_F$ and $K_L$, help to determinate the behavior of the system, but are different for each material and specific conditions [39].

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 * K_L} \qquad Eq.1$$

$$log q_e = \frac{1}{n} log C_e + log K_F \qquad Eq.2$$

In table 3 some adsorption isotherms are presented: Freundlich, Langmuir, BET, Dubinin-Radushkevich and Temkin. Each one is exposed with its original equation, which are mainly formed by constants, as presented in the table, and the value corresponding to the maximum adsorption capacity. Also, table 3 presents an example of agricultural waste that has been used to produce activated carbon and the equation used to generate its characterization.

Table 3. Adsorption isotherm models

| Isotherm | Equation | Constants | Waste | Article |
|---|---|---|---|---|
| Freundlich | $q_e = K C_e^{1/n}$ | $K_F$ n | Pecan shell | [40] |
| Langmuir | $q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$ | $K_L$ $Q_0$ | Sugarcane | [41] |
| BET | $Q_e = \frac{q_{max} K_b C_e}{(C_S - C_e)[1 + (K_b - 1)(C_e/C_S)]}$ | $q_{max}$ $K_b$ $C_S$ | Acorn shell | [42] |
| Dubinin-Radushkevich | $q_m = e^{-\beta \epsilon^2} q_e$ | $q_m$, β | Coconut shell | [43] |
| Temkin | $q_e = \frac{RT}{b_T} ln(A_T C_e)$ | $b_T$, $A_T$ | Cocoa shell | [44] |

It is important to point out that each isotherm has main applications according to the system or type of adsorption that is present in the AC. For example, Langmuir and Freundlich equations are commonly used in chemisorption and physisorption, but the first one is more useful for the analysis of a reaction mechanism, while Freundlich is easier to adjust for adsorption data. In the other hand, BET isotherm is used for multilayer physisorption as it is useful for area determination, while Temkin isotherm is applied for chemisorption systems [38,39,40,41,42].

# 4. Principal Component Analysis

*4.1. PCA introduction*

Additionally, a Principal Component Analysis (PCA) was done to study the consumer patterns of some countries corresponding to the main agricultural wastes used to produce GAC. The PCA extracts valuable information from all the presented data and expresses the information as a set of variables that are called principal components, exposing some similarity patterns of the variables and the observations by displaying them in points in graphics or maps [45].

As mentioned before, the PCA analysis assist in reducing the dimension of a data set with a large number of entries, generating interrelated variables to make the information easier to study and analyze. It is important to point out, that the uncorrelated data is not rejected, but it is presented outside of the principal components map or separated from them, so it can be understood which is correlated and which not. Besides compressing the size of the data set and extracting the most essential information of it, the PCA also simplifies the description of the statistics studied and generates an analysis of the structure of the variables or observations, helping the user to easily understand all the resulted information [46].

In order to achieve the results previously mentioned, the PCA analysis computes the new variables called principal components, which are obtained as linear combinations of the original variables presented in the data set. The first component is required to have the largest variance, so it can extract the largest part of the information, the second must be computed under the restriction of being orthogonal to the first component and to have the largest possible variance after the first component.[46].

One example of the use of this type of analysis in the industry, is an experiment developed in 2020 at Goias, Brazil, where one company wanted to know which physical and chemical attributes of tomatoes were mainly affected by the process of transportation in order to generate a higher quality in their product [47]. They analyzed firmness, titratable acidity, total soluble solid, pH and mass loss in three different stages of the process: transportation on dirt road, after transportation on dirt road and during transportation on paved road. The PCA showed a variance of 78.37% within the three principal components and generated the conclusion that titratable acidity, soluble solid and mass loss were the most affected properties as they had the higher correlations with the most representative principal component.

*4.2. PCA process and results*

To develop a PCA analysis related to the GAC, some agricultural crop productions were studied among all the countries of the World. The information was consulted in the United Nations Food and Agriculture Organization (FAO) database, which represents the tons of certain crops produced by country [18]. In this case the strategy was to use a correlation among all countries and eliminate those that presented a low interaction. It is important to point out that the database shows the information from every nation, including those who had a production of 0 tons during 2019, and for a better analysis of the information, the ones that presented more than 4 materials with zero production were eliminated from the study.

The countries resulted in the correlation for the analysis were: Brazil, China, Egypt, Germany, India, Iran, Italy, Japan, Mexico, Portugal, Switzerland, and the United States. The crops used for the analysis were almonds with shell, apricots, avocados, corn, grapes, mangoes, mangosteens, guavas, peaches and nectarines, sugar cane, sunflower seed, and walnuts with shell. It is important to point out that mangoes, mangosteens, guavas, peaches and nectarines are a single group. According to some research, all these materials were specially selected because they have a high potential to produce GAC and have been studied for some years as important raw materials with different activators.

The PC analysis was done using the software Aspen ProMV®, which initially helps to find the number of components that are suitable for the data set that resulted in the crop production of studied countries, figure 3. The results showed that using 2 components the analysis could provide reliable information where correlations factor ($R^2$) was near 1. The use of 3 components shows a value way too close to 1, but because of the third component was worth less than 0.1, does not implies a meaningful change in the results obtained with only 2 components. According to the previous, 2 components were selected for this study.

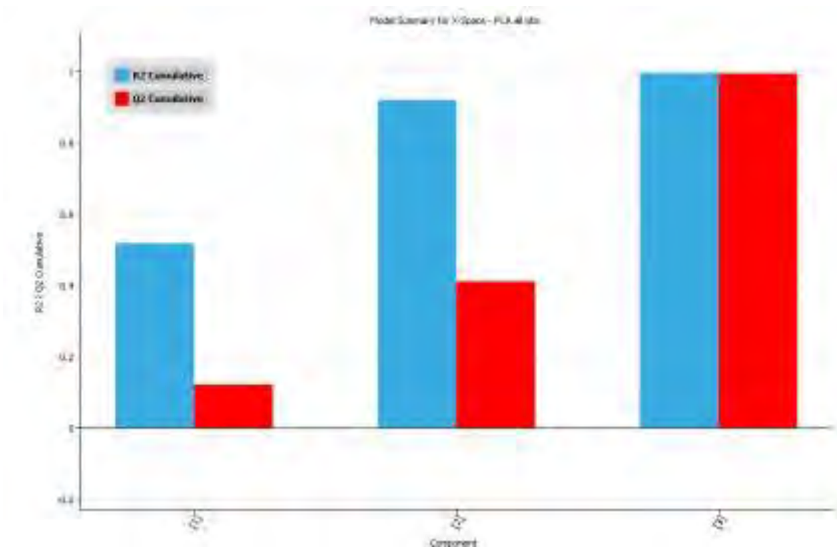


Figure 3. Component summary for PCA Aspen in ProMV®,

The figure 4 represents a biplot graph, which establishes a comparison between the production of crops and countries. As it can be seen, there is a group of crops that stick together in the center of the diagram, this means that those crops share characteristics in common. Meanwhile those crops groups separated from the country's quadrant are not recommended to be used in those countries in comparison to the ones that are still inside the circle confidence. It is important to point out that this graph does not imply that those crops should be eliminated from the study, it just determines which is better for each country. In the other hand, according to the PCA, the principal note in figure 4 is that the corn, grapes, and sugar cane were selected as the best crops for the countries studied.

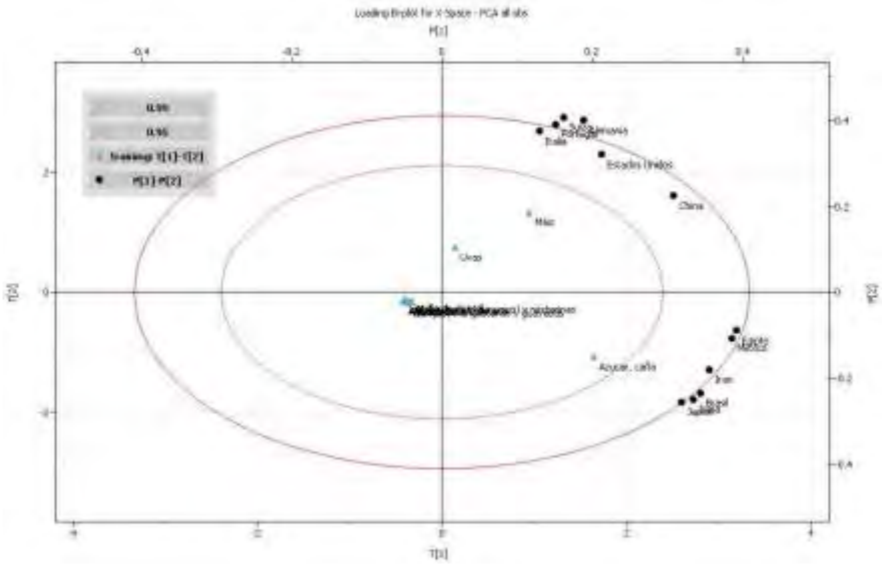


Figure 4. Biplot resulted for crops and countries in the PCA.

Another observation from figure 4 is the proximity between the crops inside the inner circle and the points that represent the countries. As showed in the biplot, some points are in the interior of the confidence circles and some are outside, this helps to understand which countries are more reliable for the study of their crops production for corn, grapes, and sugar cane. The countries that rely outside the circle are Brazil, Germany, Switzerland, and Japan as those are at the edge of the graph. Nevertheless, China, Italy and the United States presented trusted results and good interaction with corn and grapes, while Egypt, Iran and Mexico showed better results with the sugar cane production.

In figure 5, it can be seen a comparison between some of the components that were grouped in a separate quadrant, in this case the analysis is between mangoes, mangosteens, guavas, and walnuts with shell. These products were selected because of their importance of AC production during last years. As it is presented in the diagram, the countries that have a higher correlation with the first crop are Egypt, India, and México, while the ones that present a better variance with the walnuts are Iran, Switzerland, and Germany. This graph lets us understand the relation between some components and variables even when they are not the included in the main component groups.

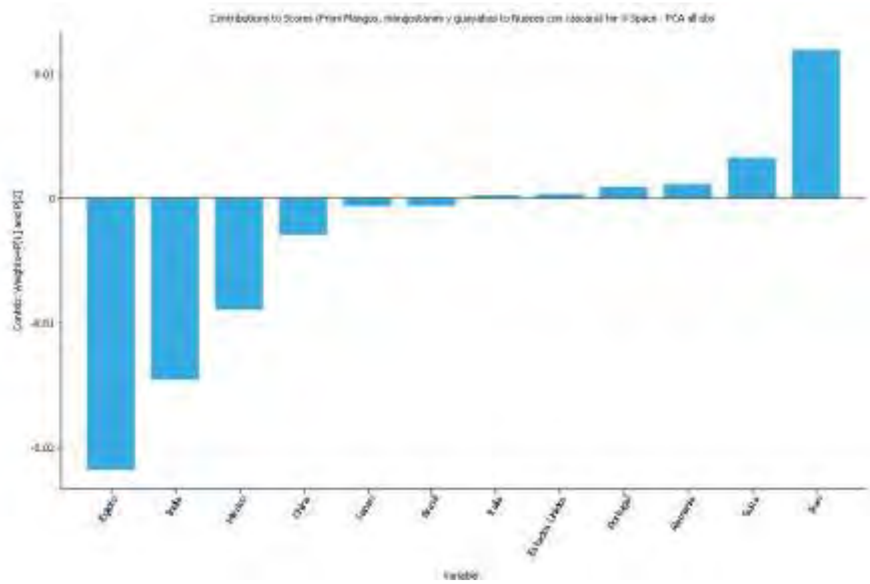


Figure 5. Country correlation comparison between mangoes, mangosteens, guavas, peaches, and nectarines; and walnuts.

# 5. Results

To start the comparison between different activators, it is important to establish the conditions used to develop each one of the GACs, in Table 4 some examples of activated carbons are exposed. Each example describes the characteristics of the process under which the initial materials were affected to obtain the desired product. This is important to point out because the use of different chemicals generates a change in the conditions of the process for each material.

For this investigation most of the raw material studied were activated using a chemical process, but some of them added an extra step with a physical stage to achieve a better result. In table 4 the process conditions are presented of the activated carbons: activation time ($t_A$) in hours, activation temperature ($T_A$), pyrolysis temperature ($T_P$), impregnation ratio (R), max adsorption ($q_{max}$) and total surface (S).

As it can be seen, the activation time is established between 2 and 4 hours, which is important because the strength of the activator can directly affect the time in which the raw material is exposed. The activation temperature is normally between 60 and 85°C, but in some cases, it can increase due to the strength of the material and considering the pH of the activator. The pyrolysis temperature is commonly suggested to be below 800°C, so the ones presented in the consulted material fulfills this topic but does change for every material and activator.

Finally, the impregnation rate is often established between 1 and 3, but it usually depends on the density of the raw material and how it reacts to the previous processes as washing, drying and activation. It is important to point out, that some of the materials are considered weak because its physical properties change during the activation as result of the contact with strong activator, presented more often in acid chemicals. Now that all the variables from the production process have been analyzed, is time to determine which activator generates better result to produce AC.

The most used activator for AC production is phosphoric acid and it represents the most part in the data obtain for this investigation, but as it can be seen there are other chemicals that can be applied to generate a good adsorbent material. To start the comparison among these activators, the first variable to study is the yield, which represents the relation between the initial mass of raw material and the final quantity of AC generated at the end of the process. This value is usually between 30-50% and is important to take in consideration because a lower number will result in a little conversion from waste to product.

While comparing the activators, the phosphoric acid presents the higher yield among the results in table 4 with a maximum value of 70.5% for pecan nutshell, followed by 52.3% and 48% for walnut shell and black cherry stones, respectively. A different paper presents a yield of 50.8% for pecan nutshell, which is still a high number to take in consideration. The first value presented for pecan nutshell is important to point out, as it means that only 29.5% of raw material is lost during the process of generating the AC, being the 32.4% the lowest value shown for phosphoric acid with the mangosteen peel.

The mangosteen peel AC activated with zinc chloride resulted in the higher value of the rest of the chemicals, with a yield of 43.5%, which is better than the phosphoric acid with the same material. It is important to point out that this last material had the same conditions with both activators, 60ºC and 3 hours during the activation process, but with the difference that the ZnCl2 had a ratio of 1 while $H_3PO_4$ used 0.5 as relation. This is essential to mention because its common that the yield decreases while the activation ratio increases, but as the chemicals are different, this means that the mangosteen peel can generate a higher yield with the zinc chloride than the phosphoric acid [55].

Some of the values that are still considered good are the grape stalks with potassium hydroxide with a total of 33.27%, macadamia shells with zinc chloride with 31.9% and again the mangosteen peel with potassium hydroxide with 31.4%. The lowest value registered is the walnut shell with potassium hydroxide as it presents 11.19%, while the same material shows a yield of 52.3% with $H_3PO_4$, showing an increase of almost 5 times and seizing more than half of the raw material instead of only a tenth of it. In the yield comparison the phosphoric acid results as the best activator having higher values that are far away from the other chemicals, excluding the mangosteen peel case where the $ZnCl_2$ showed a better outcome.

The next characteristic is the surface area, being one of the most important variables as the AC is mainly known for its adsorption capacity derived from the area available to retain pollutant molecules from the liquid or gas looking to clean. The average surface area for activated carbon is settled from 950 to 2000 $m^2/g$, being capable of adsorbing molecular weights from 100 to 1000 daltons [48].

By analyzing the data collected in table 4, the highest AC surface area produced in the reviewed articles is the sugar cane activated with potassium hydroxide, as it generated a total area of 2202 $m^2/g$, the second and third place is taken by walnut and coconut shell as main material, presenting values of 1851.1 and 1703 $m^2/g$, with phosphoric as activator. As it can be seen, two out of three of the highest values were generated by using $H_3PO_4$ with two different materials: walnut and coconut shell  While the lowest data obtained is presented by one the same materials, the coconut shell activated with sodium carbonate resulting in a small value of 494 $m^2/g$, which is positioned below the minimum values of surface area for activated carbon as it is not even close the 950 $m^2/g$ proposed by the bibliography [48].

Comparing the materials with different activators it is a huge difference between phosphoric acid and sodium carbonate with the coconut shell, presenting a variance of more than 1200 $m^2/g$ between these chemicals. Using the walnut as raw material resulted in good values for surface area, as it obtained its highest with phosphoric acid with 1851.1 $m^2/g$, followed by a total of 1689.13 $m^2/g$ with potassium hydroxide and 1223 $m^2/g$ with zinc chloride, resulting in the $H_3PO_4$ to be in top again for this material with a representative difference. Meanwhile the sugar cane presented values of 1132 and 1415 $m^2/g$ with $H_3PO_4$, which are considered good if contrasted with the 864 $m^2/g$ produced with zinc chloride, but still low compared to the 2202 $m^2/g$ obtained by the same material with KOH.

The mangosteen peel presented acceptable results with all its activators, in first place the zinc chloride showed a total of 1387 $m^2/g$, followed by potassium hydroxide with 1245 $m^2/g$, the phosphoric acid in third place with 1052 $m^2/g$ and potassium carbonate with 923 $m^2/g$, all values stay in the recommended range showed earlier except for the last one, which is below the minimum just by little. Finally, the palm shell resulted in the lowest values for surface area with a 743.71 $m^2/g$ for sodium carbonate, 642 $m^2/g$ with $H_3PO_4$ and 551.05 $m^2/g$ with zinc chloride as chemical agent.

This comparison resulted in the phosphoric acid and potassium hydroxide to be the activators that generate the highest surface in 2 materials each but resulting the first one to generate the more competitive values among the other resources. It is important to point out that the sodium carbonate generated two values below the 950 $m^2/g$, while sodium hydroxide managed to obtain a 1524 $m^2/g$ with the macadamia nutshell, which is considered satisfactory. At the same time, the phosphoric acid generated a high increase in the lowest surface area obtained, by coconut shell with sodium carbonate, from 494 $m^2/g$ to 1703 $m^2/g$, which represents a vote to the $H_3PO_4$ as activator to obtain higher surface areas.

Finally, the last variable to study and compare the chemical activators is the maximum adsorption, which is the amount of adsorbate that can be taken per mass of adsorbent, is commonly measured in mg/g. It is important to mention that in every investigation or paper the AC is produced to be tested with a certain chemical working as a pollutant, so it is not possible to compare every element from the table among each other. In the table 4, the main chemicals used to test the AC adsorption property is methylene blue and iodine, while some others are sulfuric hydroxide, methane, and chromium.

The first adsorbate to be analyzed is methylene blue, which is commonly used to determine maximum adsorption in AC studies. In this case, the main activator used is phosphoric acid with 5 samples, being the pecan nutshell the highest value for this chemical with 400 mg /g and 333 mg/g, followed by the black cherry stones with 321.75 mg/g, being the walnut shell, the worst adsorption capacity presented with 169.5 and 140.9 mg/g. Even though $H_3PO_4$ is the main activator used in the production of AC for this pollutant, the potassium hydroxide showed an important increase in this variable as it resulted in 1162.1 mg/g, which means a growth of more than 3 times the value of phosphoric acid. An important point to take in consideration, is that despite the fact that KOH has a yield of 11.19% with the walnut shell as raw material, it has an adsorption capacity of almost ten times than the one produced with $H_3PO_4$.

The next material used for adsorption studies is the iodine, which contains more activators in the samples analyzed. For this pollutant, the highest values are presented with the mangosteen peel as it has four adsorption capacities that overcome the other materials: 1240 mg/g with zinc chloride, 1100 mg/g with potassium hydroxide, 960 mg/g with phosphoric acid and 865 mg/g with potassium carbonate. It is important to mention that there is an important difference between the value produced with KOH and $H_3PO_4$, as it was the same chemical that overcome the acid in the methylene blue test. The next value close to the ones presented previously, is the sugar cane activated with phosphoric acid with a total of 746 mg/g, followed by the macadamia nutshell with zinc chloride for an adsorption of 672.4 mg/g.

In the case of adsorption of methane, the AC tested with this pollutant were the sugar cane and palm shell. The first one, activated with potassium hydroxide, produced a value of 197.23 mg/g, which can be taken as low if compared with the previous results generated by this chemical, but it is still more than ten times the value showed by palm shell activate with phosphoric acid, which offers an adsorption capacity of 19.18 mg/g of CH4. The last chemical compared as an adsorbate, is the sulfuric acid, which was tested in palm shell AC with two different activators, but presenting a value close between both agents, showing 247.33 ppm for sodium carbonate and 241.67 ppm for zinc chloride. As it can be seen, during this analysis the results presented that potassium hydroxide is the best activator, among the studied, to produce higher adsorption capacity in all materials tested, with phosphoric acid not presenting bad results but having a considerate difference with the KOH.

Table 4. AC results for different materials

| Material | Activator agent | $t_A$ (h) | $T_A$ (ºC) | R | Yield (%) | $q_{max}$ (mg/g) | S ($m^2$/g) | Source |
|---|---|---|---|---|---|---|---|---|
| Black cherry stones | Phosphoric acid | 4 | 85 | 1 | 48 | 321.75 (MB) | - | [36] |
| Coconut shell | Sodium carbonate | 4 | 160 | 5% (w/w) | - | 17.54 (PH) | 494 | [1] |
| Coconut shell | Phosphoric acid | 1 | 170 | 1 | 48 | 3.96 (Cr 3+) | 1703 | [49] |
| Grape stalks | Potassium hydroxide | - | - | 6 | 33.27 | 140.84 (Cd) | 834 | [50] |
| Macadamia nutshell | Zinc chloride | 4 | 60 | 3 | 31.9 | 672.4(I2) | | [51] |
| Macadamia nutshell | Sodium hydroxide | 2 | 130 | 3 | 30.54 | 455.33 (TC) | 1524 | [52] |
| Mangosteen peel | Phosphoric acid | 3 | 60 | 0.5 | 32.4 | 960 (I2) | 1052 | [53] |
| Mangosteen peel | Zinc chloride | 3 | 60 | 1 | 43.5 | 1240 (I2) | 1387 | [53] |
| Mangosteen peel | Potassium carbonate | 3 | 60 | 0.5 | 22.4 | 865 (I2) | 923 | [53] |
| Mangosteen peel | Potassium hydroxide | 3 | 60 | 1.5 | 31.4 | 1100 (I2) | 1245 | [53] |
| Palm shell | Phosphoric acid | 2 | 85 | 1 | - | 19.18 (CH4) | 642 | [54] |
| Palm shell | Sodium carbonate | 2 | 700 | 3 | 19.1 | 247.33 ppm (H2S) | 743.71 | [55] |
| Palm shell | Zinc chloride | 2 | 700 | 3 | 15.2 | 241.67 ppm (H2S) | 551.05 | [55] |
| Pecan nutshell | Phosphoric acid | 4 | 85 | 1.5 | 50.8 | 333 (MB) | - | [56] |
| Pecan nutshell | Phosphoric acid | 4 | 85 | 2 | 70.5 | 400 (MB) | - | [56] |
| Sugar cane | Phosphoric acid | 2 | 20 | 2 | - | 1200 (N2) | 1415 | [8] |
| Sugar cane | Phosphoric acid | 1 | 400 | 2 | 46 | 261(MB) 746 (I2) | 1132 | [57] |
| Sugar cane | Potassium hydroxide | 3 | - | 2.8 | - | 197.23 (CH4) | 2202 | [58] |
| Sugar cane | Zinc chloride | 0.5 | 80 | 0.75 | - | 24.68 (PH) | 864 | [59] |
| Walnut shell | Phosphoric acid | 4 | 85 | 1 | 41.3 | 140.8 (MB) | - | [56] |
| Walnut shell | Phosphoric acid | 4 | 85 | 2 | 52.3 | 169.5 (MB) | - | [56] |
| Walnut shell | Potassium hydroxide | 1 | 600 | 1 | 11.19 | 740(I2)1162.1(MB) | 1689.13 | [60] |
| Walnut shell | Phosphoric acid | 4 | 70 | 4 | - | 123.1(COD) | 1851.1 | [61] |
| Walnut shell | Zinc chloride | 8 | 80 | 2.5 | - | 31 (Cr VI) | 1223 | [62] |

*MB: Methylene blue, PH: Phenol, Cd: Cadmium, I2: Iodine, $CH_4$: Methane, $H_2S$: Sulfuric acid, $N_2$: Nitrogen, Cr VI: Hexavalent chromium*

# 6. Conclusions

In conclusion, the outcome demonstrates that phosphoric acid and potassium hydroxide result in the best activators for AC production as they overcame every other chemical in yield, surface area and adsorption capacity comparison.

In relation of the PCA, the study showed important information in order to develop an AC production with residues from crops used a raw material, obtaining that corn, grape and sugar cane were the best materials as they showed a better relationship with the selected countries from the study. Additionally, using the biplot diagram produced from the PCA, it is possible to conclude that the sugar cane generated a better relationship with Egypt, Iran and Mexico, while the corn and grapes is settled for China, Italy and the United States.

The results obtained in this study show an important comparison between the main variables that determine the quality of AC. Regardless of the reliability of this article, the comparison can be improved by developing a production of AC using different materials with various activators and applying the same conditions during the process, compare and generate a well-founded contrast among the chemicals and evaluate each variable in a deeper approach.

The results of the yield analysis, showed that the $H_3PO_4$ presented values above the maximum acceptable (50%), producing a 70.5% with pecan nutshell and 52.3% with walnut shell, generating an important reduction in the raw material loss. For the surface area category, the KOH had an interesting outcome as it ended up being the best activator, obtaining the highest value with 2202 $m^2/g$, overcoming the normal range for a representative amount, even though the $H_3PO_4$ came after this activator, it showed acceptable result for this variable with most of the materials. Finally, for the adsorption capacity, the KOH generated better products in general and having a representative advantage over the $H_3PO_4$, which obtained constant and stable results, providing adequate values for all materials as well.

# 7. References

[1] R. Desmiarti, Y. Trianda, M. Martynis, A. Viqri, T. Yamada, and F. Li, “Phenol adsorption in water by granular activated carbon from coconut shell,” *Int. J. Technol.*, vol. 10, no. 8, pp. 1488–1497, 2019, doi: 10.14716/ijtech.v10i8.3463.

[2] D. C. S. Azevedo, J. C. S. Araújo, M. Bastos-Neto, A. E. B. Torres, E. F. Jaguaribe, and C. L. Cavalcante, “Microporous activated carbon prepared from coconut shells using chemical activation with zinc chloride,” *Microporous Mesoporous Mater.*, vol. 100, no. 1–3, pp. 361–364, 2007, doi: 10.1016/j.micromeso.2006.11.024.

[3] K. Selvi, S. Pattabhi, and K. Kadirvelu, “Removal of Cr(VI) from aqueous solution by adsorption onto activated carbon,” *Bioresour. Technol.*, vol. 80, no. 1, pp. 87–89, 2001, doi: 10.1016/S0960-8524(01)00068-2.

[4] V. Selvaraj, T. R. Raghavarshini, and M. Alagar, “Development and Characterization of Palm Flower Carbon Reinforced DOPO-Urea Diamine Based Cardanol Benzoxazine-Epoxy Hybrid Composites,” *Polym. Eng. Sci.*, vol. 60, no. 4, pp. 732–739, 2020, doi: 10.1002/pen.25331.

[5] M. K. Al Mesfer, “Synthesis and characterization of high-performance activated carbon from walnut shell biomass for CO2 capture,” *Environ. Sci. Pollut. Res.*, pp. 1–9, 2020.

[6] M. A. Zazouli, D. Naghipour, S. Heydari, and S. D. Ashrafi, “Adsorptive Removal of Bisphenol A From Aqueous Solutions by Activated Carbon Derived From Walnut Shells: Optimization by Response Surface Methodology,” *Casp. J. Heal. Res.*, vol. 4, no. 3, pp. 66–71, 2019, doi: 10.29252/cjhr.4.3.66.

[7] Y. Cai, L. Liu, H. Tian, Z. Yang, and X. Luo, “Adsorption and Desorption Performance and Mechanism of Tetracycline Hydrochloride by Activated Carbon-Based Adsorbents Derived from Sugar Cane Bagasse Activated with ZnCl2.”

[8] F. M. T. Mendes, A. C. C. Marques, D. L. Mendonça, M. S. Oliveira, R. O. Moutta, and V. S. Ferreira-Leitão, “High Surface Area Activated Carbon from Sugar Cane Straw,” *Waste and Biomass Valorization*, vol. 6, no. 3, pp. 433–440, 2015, doi: 10.1007/s12649-015-9356-5.

[9] L. Ma, J. Li, and X. Ma, “Preparation and adsorption of CO2 and H2 by activated carbon hollow fibers from rubber wood (Hevea brasiliensis),” *BioResources*, vol. 14, no. 4, pp. 9755–9765, 2019, doi: 10.15376/biores.14.4.9755-9765.

[10] O. A. Habeeb, O. A. Olalere, R. Kanthasamy, and B. V. Ayodele, “Hydrogen Sulfide Removal from Downstream Wastewater Using Calcium-Coated Wood Sawdust-Based Activated Carbon,” *Arab. J. Sci. Eng.*, vol. 45, no. 2, pp. 501–518, 2020, doi: 10.1007/s13369-019-04207-9.

[11] E. Vunain, D. Houndedjihou, M. Monjerezi, A. A. Muleja, and B. T. Kodom, “Adsorption, Kinetics and Equilibrium Studies on Removal of Catechol and

Resorcinol from Aqueous Solution Using Low-Cost Activated Carbon Prepared from Sunflower (Helianthus annuus) Seed Hull Residues," *Water. Air. Soil Pollut.*, vol. 229, no. 11, 2018, doi: 10.1007/s11270-018-3993-9.

[12] A. A. Donaldson, P. Kadakia, M. Gupta, and Z. Zhang, "Production of energy and activated carbon from agri-residue: Sunflower seed example," *Appl. Biochem. Biotechnol.*, vol. 168, no. 1, pp. 154–162, 2012, doi: 10.1007/s12010-011-9358-0.

[13] R. C. Bansal and M. Goyal, "Activated carbon adsorption," *Act. Carbon Adsorpt.*, no. May, pp. 1–472, 2005, doi: 10.1680/bwtse.63341.147.

[14] United Nations, "The sustainable development goals report 2019," *United Nations Publ. issued by Dep. Econ. Soc. Aff.*, p. 64, 2019, [Online]. Available: https://undocs.org/E/2019/68.

[15] SIAP, "Anuario Estadístico de la Producción Agrícola.," 2020. .

[16] SEMARNAT, "Residuos Sólidos Urbanos." https://www.gob.mx/semarnat/acciones-y-programas/residuos-solidos-urbanos-rsu.

[17] Secretaría de Energía, "Atlas Nacional de Biomasa," 2020, [Online]. Available: https://dgel.energia.gob.mx/anbio/.

[18] Food and Agriculture Organization from the United Nations, "FAOSTAT," 2020. http://www.fao.org/faostat/en/#data (accessed Jul. 21, 2020).

[19] European Commission, *Impacts and achievements of bioenergy projects supported under the EU programme IEE II - Summary report*. 2016.

[20] J. Bedia, M. Peñas-Garzón, A. Gómez-Avilés, J. J. Rodriguez, and C. Belver, "Review on Activated Carbons by Chemical Activation with FeCl3," *C — J. Carbon Res.*, vol. 6, no. 2, p. 21, 2020, doi: 10.3390/c6020021.

[21] J. M. Dias, M. C. M. Alvim-Ferraz, M. F. Almeida, J. Rivera-Utrilla, and M. Sánchez-Polo, "Waste materials for activated carbon preparation and its use in aqueous-phase treatment: A review," *J. Environ. Manage.*, vol. 85, no. 4, pp. 833–846, 2007, doi: 10.1016/j.jenvman.2007.07.031.

[22] N. Ye, Z. Wang, S. Wang, and W. J. G. M. Peijnenburg, "Toxicity of mixtures of zinc oxide and graphene oxide nanoparticles to aquatic organisms of different trophic level: particles outperform dissolved ions," *Nanotoxicology*, vol. 12, no. 5, pp. 423–438, 2018, doi: 10.1080/17435390.2018.1458342.

[23] Elsevier, "Scopus," 2020. https://www-scopus-com.udlap.idm.oclc.org/search/form.uri?display=basic#basic (accessed Nov. 30, 2020).

[24] Secretaría de Economía, "Perfil del carbón," 2012.

[25] D. Chen, Y. Wang, and Y. Zou, "Activated carbon fiber fabrics in filtration and clean water resources," *Mater. Sci. Forum*, vol. 980, pp. 387–393, 2020, doi:

10.4028/www.scientific.net/MSF.980.387.

[26] F. Cecen and Ö. Aktas, *Activated Carbon for Water and Wastewater Treatment: Integration of Adsorption and Biological Treatment*, John Wiley. 2011.

[27] M. Martin-Martinez, L. M. Gómez-Sainero, M. A. Alvarez-Montero, J. Bedia, and J. J. Rodriguez, "Comparison of different precious metals in activated carbon-supported catalysts for the gas-phase hydrodechlorination of chloromethanes," *Appl. Catal. B Environ.*, vol. 132–133, pp. 256–265, 2013, doi: 10.1016/j.apcatb.2012.11.041.

[28] D. Qu, "Studies of the activated mesocarbon microbeads used in double-layer supercapacitors," *J. Power Sources*, vol. 109, no. 2002, pp. 403–411, 2002.

[29] M. Boehler, B. Zwickenpflug, J. Hollender, T. Ternes, A. Joss, and H. Siegrist, "Removal of micropollutants in municipal wastewater treatment plants by powder-activated carbon," *Water Sci. Technol.*, vol. 66, no. 10, pp. 2115–2121, 2012, doi: 10.2166/wst.2012.353.

[30] J. F. Kwiatkowski, "Activated carbon: Classifications, properties and applications," *Activated Carbon: Classifications, Properties and Applications*. pp. 1–555, 2011.

[31] A. C. Lua, F. Y. Lau, and J. Guo, "Influence of pyrolysis conditions on pore development of oil-palm-shell activated carbons," *J. Anal. Appl. Pyrolysis*, vol. 76, no. 1–2, pp. 96–102, 2006, doi: 10.1016/j.jaap.2005.08.001.

[32] Y. Sun and P. A. Webley, "Preparation of activated carbons from corncob with large specific surface area by a variety of chemical activators and their application in gas storage," *Chem. Eng. J.*, vol. 162, no. 3, pp. 883–892, 2010, doi: 10.1016/j.cej.2010.06.031.

[33] I. N. Najm, V. L. Snoeyink, B. W. Lykins, and J. Q. Adams, "Using Powdered Activated Carbon: A Critical Review," *J. Am. Water Works Assoc.*, vol. 83, no. 1, pp. 65–76, 1991, doi: 10.1002/j.1551-8833.1991.tb07087.x.

[34] Karen J. Peña H.; Liliana Giraldo; Juan Carlos Moreno, "Preparação De Carvão Ativado De Casca De Laranja Por," *Rev. Colomb. Química*, vol. 41(2), pp. 311–323, 2012, [Online]. Available: http://www.scielo.org.co/scielo.php?script=sci_arttext&pid=S0120-28042012000200010.

[35] H. Marsh and F. Rodríguez-Reinoso, *Activated Carbon*, 1st. Editi. Elsevier Science, 2006.

[36] J. M. Ramos-Rodríguez and R. Reyes Mazzoco, "Adsorption studies of methylene blue and phenol onto black stone cherries prepared by chemical activation," *J. Hazard. Mater.*, vol. 180, no. 1–3, pp. 656–661, 2010, doi: 10.1016/j.jhazmat.2010.04.086.

[37] S. M. Yakout and G. Sharaf El-Deen, "Characterization of activated carbon prepared

by phosphoric acid activation of olive stones,” *Arab. J. Chem.*, vol. 9, pp. S1155–S1162, 2016, doi: 10.1016/j.arabjc.2011.12.002.

[38] L. Zhou, *Adsorption: Progress in Fundamental and Application Research*. Tianjin,China: World Scientific, 2007.

[39] S. D. Faust and O. M. Aly, *Chemistry of water treatment*. Boston, 1983.

[40] C. Ng, J. N. Losso, W. E. Marshall, and R. M. Rao, “Freundlich adsorption isotherms of agricultural by-product-based powdered activated carbons in a geosmin-water system,” *Bioresour. Technol.*, vol. 85, no. 2, pp. 131–135, 2002, doi: 10.1016/S0960-8524(02)00093-7.

[41] W. T. Tsai, C. Y. Chang, M. C. Lin, S. F. Chien, H. F. Sun, and M. F. Hsieh, “Adsorption of acid dye onto activated carbons prepared from agricultural waste bagasse by ZnCl2 activation,” *Chemosphere*, vol. 45, no. 1, pp. 51–58, 2001, doi: 10.1016/S0045-6535(01)00016-9.

[42] C. Saka, “BET, TG-DTG, FT-IR, SEM, iodine number analysis and preparation of activated carbon from acorn shell by chemical activation with ZnCl2,” *J. Anal. Appl. Pyrolysis*, vol. 95, no. March, pp. 21–24, 2012, doi: 10.1016/j.jaap.2011.12.020.

[43] D. Mohan, K. P. Singh, and V. K. Singh, “Trivalent chromium removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth,” *J. Hazard. Mater.*, vol. 135, no. 1–3, pp. 280–295, 2006, doi: 10.1016/j.jhazmat.2005.11.075.

[44] T. Chinniagounder, M. Shanker, and S. Nageswaran, “Adsorptive Removal of Crystal Violet Dye Using Agricultural Waste Cocoa ( theobroma cacao ) Shell,” *Res. J. Chem. Sci.*, vol. 1, no. 7, pp. 38–45, 2011.

[45] I. T. Jollife and J. Cadima, “Principal component analysis: A review and recent developments,” *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.*, vol. 374, no. 2065, 2016, doi: 10.1098/rsta.2015.0202.

[46] H. Abdi and L. J. Williams, “Principal component analysis,” *Wiley Interdiscip. Rev. Comput. Stat.*, vol. 2, no. 4, pp. 433–459, 2010, doi: 10.1002/wics.101.

[47] T. de A. Machado, A. G. Costa, R. E. Rodrigues, M. A. dos Santos, A. C. de L. Ribeiro, and C. A. Megguer, “Quality of tomatoes under different transportation conditions by principal component analysis,” *Rev. Ceres*, vol. 67, no. 6, pp. 448–453, 2020, doi: 10.1590/0034-737x202067060004.

[48] J. Da Lu and J. Xue, *Poisoning: Kinetics to Therapeutics*, Third Edition. 2019.

[49] D. Higai, Z. Huang, and E. W. Qian, “Preparation and surface characteristics of phosphoric acid-activated carbon from coconut shell in air,” *Environ. Prog. Sustain. Energy*, vol. 40, no. 2, 2021, doi: 10.1002/ep.13509.

[50] Z. H. Shahraki, H. Sharififard, and A. Lashanizadegan, “Grape stalks biomass as raw material for activated carbon production: Synthesis, characterization and adsorption

ability," *Mater. Res. Express*, vol. 5, no. 5, 2018, doi: 10.1088/2053-1591/aac1cd.

[51] N. Dejang, O. Somprasit, and S. Chindaruksa, *A Preparation of Activated Carbon from Macadamia Shell by Microwave Irradiation Activation*, vol. 79. Elsevier B.V., 2015.

[52] A. C. Martins *et al.*, "Removal of tetracycline by NaOH-activated carbon produced from macadamia nut shells: Kinetic and equilibrium studies," *Chem. Eng. J.*, vol. 260, pp. 291–299, 2015, doi: 10.1016/j.cej.2014.09.017.

[53] L. Giraldo, P. Rodriguez-Estupiñan, and J. C. Moreno-Piraján, "A microcalorimetric study of methane adsorption on activated carbons obtained from mangosteen peel at different conditions," *J. Therm. Anal. Calorim.*, vol. 132, no. 1, pp. 525–541, 2018, doi: 10.1007/s10973-018-6958-8.

[54] A. Arami-Niya, W. M. A. Wan Daud, F. S. Mjalli, F. Abnisa, and M. S. Shafeeyan, "Production of microporous palm shell based activated carbon for methane adsorption: Modeling and optimization using response surface methodology," *Chem. Eng. Res. Des.*, vol. 90, no. 6, pp. 776–784, 2012, doi: 10.1016/j.cherd.2011.10.001.

[55] K. Hussaro and Rattanakosin, "PREPARATION OF ACTIVATED CARBON FROM PALM OIL SHELL BY CHEMICAL ACTIVATION WITH Na2CO3 AND," *Am. J. Environ. Sci.*, vol. 101, no. 4, pp. 177–185, 2014, doi: 10.3844/ajessp.2014.

[56] V. Bello-Huitle, P. Atenco-Fernández, and R. Reyes-Mazzoco, "Adsorption studies of methylene blue and phenol onto pecan and castile nutshells prepared by chemical activation," *Rev. Mex. Ing. Quim.*, vol. 9, no. 3, pp. 313–322, 2010.

[57] J. B. Castro, P. R. Bonelli, E. G. Cerrella, and A. L. Cukierman, "Phosphoric acid activation of agricultural residues and bagasse from sugar cane: Influence of the experimental conditions on adsorption characteristics of activated carbons," *Ind. Eng. Chem. Res.*, vol. 39, no. 11, pp. 4166–4172, 2000, doi: 10.1021/ie0002677.

[58] J. Sreńscek-Nazzal, W. Kamińska, B. Michalkiewicz, and Z. C. Koren, "Production, characterization and methane storage potential of KOH-activated carbon from sugarcane molasses," *Ind. Crops Prod.*, vol. 47, pp. 153–159, 2013, doi: 10.1016/j.indcrop.2013.03.004.

[59] D. Kalderis *et al.*, "Adsorption of polluting substances on activated carbons prepared from rice husk and sugarcane bagasse," *Chem. Eng. J.*, vol. 144, no. 1, pp. 42–50, 2008, doi: 10.1016/j.cej.2008.01.007.

[60] X. Li *et al.*, "Characterization and comparison of walnut shells-based activated carbons and their adsorptive properties," *Adsorpt. Sci. Technol.*, vol. 38, no. 9–10, pp. 450–463, 2020, doi: 10.1177/0263617420946524.

[61] A. R. Mahdavi, A. A. Ghoresyhi, A. Rahimpour, H. Younesi, and K. Pirzadeh, "COD removal from landfill leachate using a high-performance and low-cost activated carbon synthesized from walnut shell," *Chem. Eng. Commun.*, vol. 205, no.

9, pp. 1193–1206, 2018, doi: 10.1080/00986445.2018.1441831.

[62] M. Ghasemi, A. A. Ghoreyshi, H. Younesi, and S. K. Khoshhal, “Synthesis of a high characteristics activated carbon from walnut shell for the removal of Cr (VI) and Fe (II) from aqueous solution: single and binary solutes adsorption,” *Iran. J. Chem. Eng.*, vol. 12, no. 4, pp. 28–51, 2015, [Online]. Available: http://www.ijche.com/article_11697.html%0Ahttp://www.ijche.com/pdf_11697_cd9243a5e5b63effca87f75f9cda007b.html.