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Preparation and Characterization of Activated Carbon Monoliths with Potential Application as Phenol Adsorbents

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Abstract: A series of different activated carbons of both honeycomb and disc type were prepared by chemical activation of coconut shells with zinc chloride at different concentrations, without the use of a binder. The structures were characterized by N₂ adsorption at 77 K and scanning electron microscopy (SEM), and also some samples were characterized by immersion calorimetry in benzene. These were subsequently used in the adsorption of phenol in aqueous solution. The experimental results indicate that activation with zinc chloride produced a large development of microporosity with a micropore volume of 0.38 to 0.79 cm³ g⁻¹, BET area between 725 and 1523 m² g⁻¹ and the capacity to adsorb phenol. In addition, the BET and Langmuir models were applied to isotherm data.

Keywords: Chemical activation, honeycomb, Coconut shells, Carbon monoliths, Phenol adsorption.

Introduction

In recent decades, alternative technologies have been developed for reducing pollution in gaseous and liquid phases. Solutions such as the use of granular activated carbon (GAC), powder activated carbon (PAC), fibers carbon (FAC) and activated carbon monoliths (ACM), among others, have been widely implemented due to the increasing demand and great versatility of these materials. The characteristics of ACM have resulted in it being termed a "new material" and it has been used in a wide range of areas such as the operation of air conditioning systems, in supporting the catalytic and the chemical industry in the removal of compounds such as benzene, acetone, dichloromethane, hexane and acrylonitrile,

among others^{1,2}. The porous structure of the ACM is made up mostly by micropores, whereas other activated carbons have a complex structure consisting of micropores, mesopores and macropores. The word "monolith" means "one stone" and refers to compact structures such as monoliths of the disc and honeycomb types. The latter are unit structures crossed lengthwise by parallel canals² and constitute a new concept in the design of catalysts and adsorbents. This has allowed major innovations to emerge in recent decades. These new structures offer low values drop to the passage of gases, facilitating the uniform flow of the same, excellent mechanical properties, a large surface area per unit weight or volume and they also behave like most adiabatic systems and reduce the constraints generated by the phenomenon of internal diffusion². When comparing the properties of monolithic catalysts with those of catalysts with more conventional forms (cylinders, spheres, rings, *etc.*), it was found that the compact structure not only facilitates management but allows freedom of orientation in the reactor and significantly reduces the problems of the restriction granular catalysts³.

These structures can be synthesized from materials such as γ -alumina, silica, titanium oxide, cordierite and lignocellulosic materials, among others. The latter generate monoliths that can potentially be used as direct adsorbents or catalytic supports, and studies have increased to establish appropriate conditions for synthesis. The aim of this study was to assess the preparation of activated carbon monoliths (ACM) of honeycomb and disc types from coconut shells, through chemical activation with zinc chloride (ZnCl_2) and formation by pressing without the use of a binder⁴. The structures were characterized by determining N_2 adsorption isotherms at 77 K, scanning electron microscopy and immersion calorimetry in benzene. Additional tests were performed with the ACM to determine their phenol adsorption capacity in aqueous solutions.

Experimental

Figure 1 represents the ACM synthesis process.

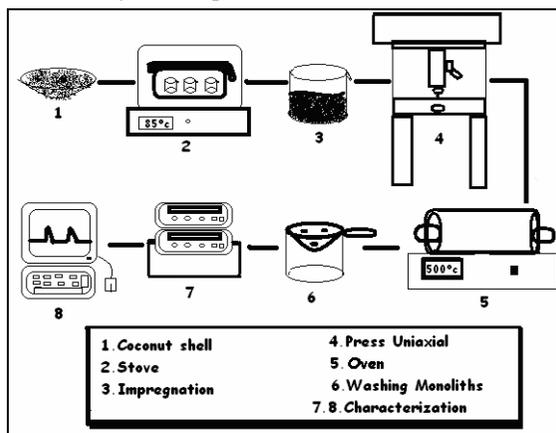


Figure 1. The monolith synthesis process.

Preparation and characterization of the precursor material

The coconut shell was ground and sieved for the synthesis process using a particle size of 38 μM . In order to establish its behavior under different temperatures, the raw material was impregnated and subjected to thermogravimetric analysis (TGA)⁵. The sample analysis was undertaken using NETZSCH STA 409 PC / PG, and for this purpose 94.70 mg of coconut shell was used, with a flow of N_2 1 mL min^{-1} and a temperature range between 303 K and 1 373 K.

Activated carbon disc and honeycomb synthesis

The precursor was impregnated with a desiccating agent, in this case zinc chloride, at 1 g of precursor for 2 mL of solution, for 7 h at 358 K, followed by drying at 383 K for about 2 h. Then carry a press axial, which was formed by pressing at 423 K at a pressure of 4500 psi. These structures were then carbonized in an oven at a temperature of 773 K, a N₂ flow of 85 mL min⁻¹ and a heating rate of 274 K min⁻¹ for 2 h. Finally, they were washed with 0.1 M hydrochloric acid and distilled water until a neutral pH was reached, to eliminate the remnants of the chemical agents used during impregnation⁶.

Different ZnCl₂ concentrations (20%, 32%, 48%) were used to prepare the monolith series, symbolized by the letters MFD1 for disks and MFH2 for honeycombs, followed in each case by the concentration used for each series (MFD120, MFD132, MFD148, MFH220, MFH232, MFH248). Other conditions were maintained as constant. The relative impregnation values for each set are 0.19, 0.30 and 0.46 respectively.

Characterization of the structures

All activated carbon monoliths were characterized by physical adsorption of N₂ to 77 K using the Quantachrome, Autosorb 3-B. The microporous volume was estimated by applying the Dubinin-Radushkevich equation and the surface area was obtained using the BET method. Some samples were characterized by immersion calorimetry in benzene (0.37 nm), using Calvet-type equipment⁷ and scanning electron microscopy (SEM).

Determination of the phenol adsorption capacity from aqueous solutions

Calibration curves of absorbance, depending on the phenol concentration in the aqueous solutions, at a wavelength of 269 nm were determined. To determine the phenol adsorption of the activated carbon monoliths, 500 mg of solids were placed in glass bottles with 50 mL of a phenol aqueous solution (of 500 and 1500 mgL⁻¹) and the solutions were adjusted to pH 7. The samples were shaken mechanically and kept at a temperature of 298 K, for a period of approximately 48 h. The residual phenol concentration in the solutions after adsorption was determined by spectrophotometric UV-Vis, Milton Roy Co. Spectronic Genesys SN.

Results and Discussion*Thermogravimetric analysis (TGA)*

Figure 2 represents the analysis undertaken for raw coconut shell and coconut shell impregnated with 20%, 32% and 48% of ZnCl₂. From the TGA obtained for coconut shell raw it can be seen that between 323 K and 453 K there was a loss of 10.27% of the initial mass in relation to the elimination of moisture from the sample in addition to moisture also removed by volatile compounds, which are carried by the steam flow that comes from biomass during the evaporation process. This is consistent with the behavior of the DTA which indicates an endothermic process of water evaporation. At temperatures above 493 K, the thermogravimetric registration slope changed significantly, indicating the beginning of the carbonization process caused by the vaporization of the volatile compounds. At a temperature of 574 K, a 22.63% loss in mass occurred. In the temperature range of 493 K and 603 K, an increasing loss of the materials was observed due to components that were torn away from the amorphous structure more easily due to the effects of temperature. Between 603 K and 723 K, the maximum values of mass loss occurred, obtaining a solid residue virtually without volatile compounds, but still with an incomplete carbonization degree inside the samples. In a subsequent temperature interval higher than 673 K, another change occurs on the slopes of the

thermogravimetric records: temperatures in the range of 574 K to 773 K produce the main mass loss of 66.56% which is a result of the cellulose thermal degradation that occurs in two stages. First, there is a downsizing of the cellulose chain due to the severance of links from the generation of free radicals, carboxylic groups and carbonyls, as well as the formation of carbon, while the second stage includes cellulose depolymerization due to breakage of glucoside units and the formation of levoglucosan. Decomposition above 683 K is attributed to the degradation of cellulose and lignin, the main components of lignocellulosic materials⁸ and that coincides with the peak of the maximum zone of heat flow. Weight loss with respect to the initial mass continued, but this time at a very high temperature until soft. Between 773 K and 1073 K there was a loss of over 70.86% and in the range of 1073 K to 1099 K the remaining mass was 28.75%, which indicates a loss of just 1.33% over a considerable range of 572 K. The fixed carbon content, in the waste product that was carbonized, increased with rising temperatures, becoming a solid porous mass. The observed correspondence with the thermogravimetric registration slope (Figure 2) illustrates that in the intervals between 493 K and 723K, approximately 66% of the mass loss occurred. At pyrolysis temperatures above 723 K will arise charred of appropriate conditions for the subsequent adsorbents synthesis⁹, recommending the use of a low heating rate to avoid drastic morphological damage during the pyrolysis process and subsequent activation.

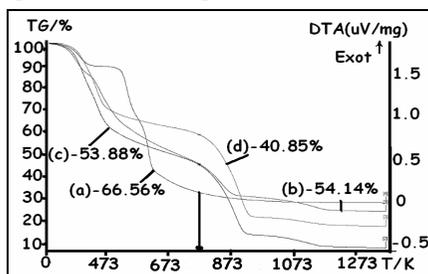


Figure 2. Thermogravimetric analysis of raw coconut shell and with impregnation of ZnCl_2 (a) raw (b) 20% ZnCl_2 (c) 32% ZnCl_2 and (d) 48% ZnCl_2 .

Following the TGA, the coconut shell was impregnated with the aforementioned concentrations and analysis was focused on the temperature of 773 K. It was noted that in general, at greater concentrations of impregnating agent, there was a minor loss of mass and therefore more structure available for the carbonization process. This was illustrated by the mass loss rate at this point (raw - 66.56% [20%] - 54.14% [32%] - 53.88% [48%] - 40.85%) and at the same time, the process of dehydration increased sharply with the impregnation and a minor release of volatile materials under increasing concentration of ZnCl_2 occurred. Therefore more tars are available on the surface to set the carbon and improve the performance of the process¹⁰, which was observed by the slope of each thermogram. A temperature of 773 K shows a mass loss of approximately 50%, which makes it possible to obtain a porous solid with good characteristics.

The characteristics of the structures

Figure 3 shows that isotherms obtained for the honeycomb and discs types illustrate the synthesis of microporous structures with a good surface area and micropore volume. The isotherms are type I solids with large micropores, which have surface areas between 725 and 1523 m^2g^{-1} and a microporous volume between 0.39 and 0.79 cm^3g^{-1} . These results are satisfactory, taking into account that under similar synthesis conditions surface areas between 500 and 2000 m^2g^{-1} have been obtained⁶, together with a microporous volume of between 0.2 - 1 cm^3g^{-1} .

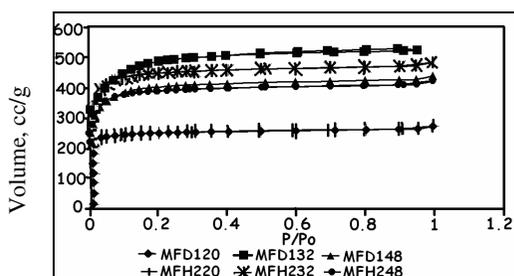


Figure 3. N₂ adsorption isotherms to 77 K of honeycombs and disc at different concentrations of ZnCl₂.

Table 1 shows that yield of carbonization increase with increase of concentrations of the impregnating agent. This fact is agree with the results obtained of TGA for different samples, since a major concentration of impregnation agent more residual mass available in the carbonization. The heating process during pressing reduced the loss of volatile matter and increases the resistance of porous solids synthesized. Finally, during heat treatment the impregnating agent acts as a drying agent that favor the release of hydrogen and oxygen into the interior in the form of H₂O, COx or hydrocarbons

Table 1. Characteristics of the synthesized ACM.

Series Monoliths	Relationship of impregnation	Microporous Volume DR cm ³ /g	Área BET m ² /g	Yield
MFH220	0,19	0,39	726	45,94%
MFH232	0,30	0,72	1 315	50,83%
MFH248	0,46	0,62	1 170	53,71%
MFD120	0,19	0,45	821	35,09%
MFD132	0,30	0,79	1 523	45,05%
MFD148	0,46	0,65	1 206	51,93%

Table 2. Characteristics of the synthesized ACM (Immersion enthalpy and adsorption of phenol).

Series Monoliths	-ΔH _{imm} J.g ⁻¹	Quantity of phenol adsorbed, mg.g ⁻¹	1500 ppm	500 ppm
MFD120	30.71		24.04	7.38
MFD132	42.63		78.05	32.41
MFD148	36.95		55.52	22.32
MFH220	25.23		39.69	20.09
MFH232	38.16		108.61	35.91
MFH248	35.19		93.61	31.33

This impregnation agent penetrates into the interior of the particles producing a partial fragmentation of cellulose and other biopolymers of plant structures such as lignin and hemicelluloses. The reactions that followed were dehydration and condensation and enabled more aromatic compounds to be produced with the appearance of tar, which remained on the particle surface, impregnated and acted as a binder¹¹. Due to this it was not necessary to use any material that agglomerates the precursor particles, so the porosity was not affected by the presence of the binder after carbonization. As a result of precursor impregnation with ZnCl₂, the mass deformed with the pressure, allowing the reduction of space between particles. This data was obtained from the N₂ adsorption isotherms used in the application of two models of gas adsorption, BET and Langmuir. Figures 4 & 5 show a linear trend of the data revealed by good correlation coefficients of around 0.9995-0.9998.

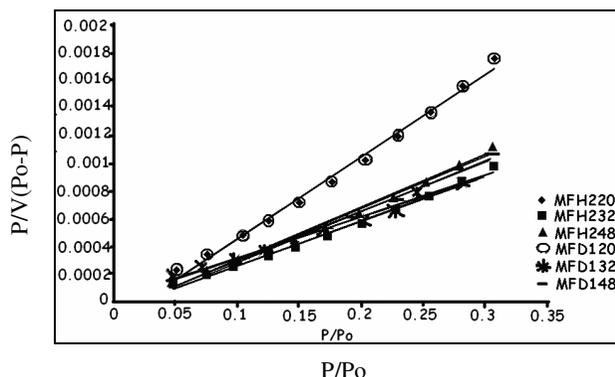


Figure 4. Representation of the BET model for the series of synthesized monoliths.

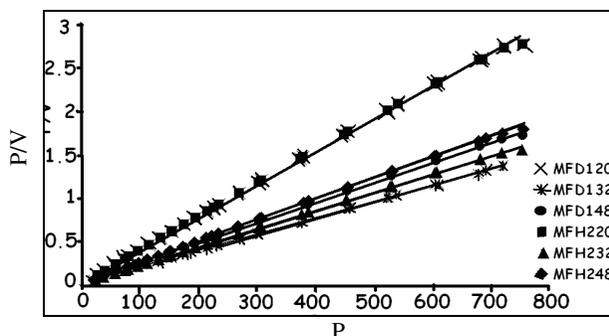


Figure 5. Representation of the Langmuir model for the series of synthesized monoliths.

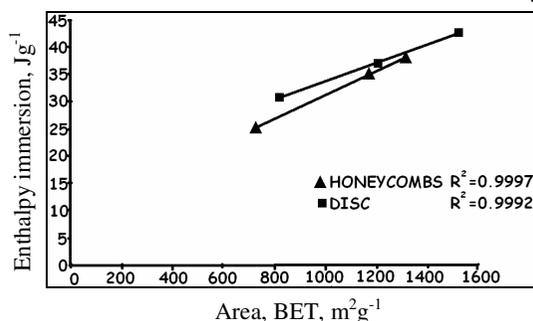
The characteristic data of the BET and Langmuir models is shown in Table 3. When comparing the values of V_m a marked trend can be observed between the two models. The V_m values obtained from the BET model are lower than those calculated by the Langmuir model, and are independent of the considered adsorption^{12,13}. But in both cases V_m increases with the surface area of the ACM. In Figure 5, it is shown that the Langmuir model is sensitive to variations in the carbon porosity, thus for carbons with a greater porosity (MFD132, MFH232) the slope is less steep than for carbons with a lower porosity (MFD120, MFH220) although activated carbons fit straight model to Langmuir representations, the point in coordinate Y was both, displaced to minor pressure, when the microporosity of carbon is broader and the slope of the straight stretch at higher pressures, decreases in the same direction¹⁴. Also it can be noted that parameter K, which is between 0.068 and 0.100 for all samples, is sensitive to changes in carbon microporosity, being so much while more micropores is the carbon such that the series MFH232, which has a pore volume of 0.79, presents the greatest K value of 0.1.

Two constants characterize the equation isotherm of BET: V_m , which is the adsorption capacity in the monolayer and C, constant energy, which is a parameter associated with the difference between energy adsorption of the molecules in the first layer and the other remaining layers. Table 3 illustrates the change in parameter C in the series of synthesized monoliths of a range between 42 and 331, being higher in samples MFD132 and MFH32. This coincides with the main phenol adsorption capacity of these samples in comparison to the other samples and is a consistent behavior since parameter C gives an idea of the molecules residence time on the surface. When C is large, the residence time of adsorbate is longer, which indicates a high potential for interaction on the surface and consequently a significant heterogeneity energetic¹⁴.

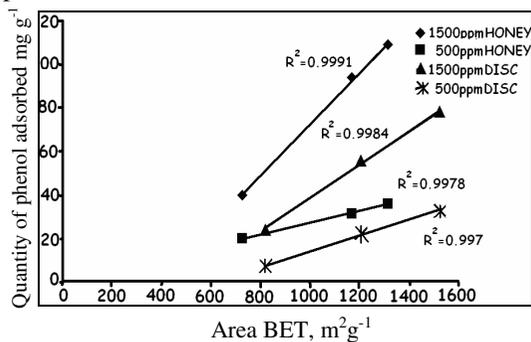
Table 3. Characteristics of the synthesized ACM (Models BET and Langmuir).

Series Monoliths	Model langmuir	$V_m, \text{cm}^3 \cdot \text{g}^{-1}$	K	Model Bet	$V_m, \text{cm}^3 \cdot \text{g}^{-1}$	C
MFD120	Model langmuir	270.27	0.096	Model Bet	188.68	53
MFD132		526.31	0.068		349.65	146
MFD148		434.78	0.082		277.01	42
MFH220		270.27	0.096		166.67	60
MFH232		476.19	0.100		302.11	331
MFH248		416.66	0.094		268.82	49

The immersion enthalpy is indicative of the interaction between solids and the immersion liquid, which in this work was the phenol aqueous solution. The value of this property corresponds to the total quantity of heat generated in the solute adsorption process, and therefore also implies interaction with the solvent. In Table 2, showing the immersion enthalpy values of the ACM in benzene, the immersion enthalpy values obtained for the different sets of discs and honeycombs show that a main area BET greater immersion enthalpy (Figure 6) being this agree and that there is greater surface area ready to interact with the adsorbate. The correlation coefficients show that the data are consistent with the linearity.

**Figure 6.** Immersion enthalpy of the monoliths honeycomb and disc in benzene in the BET area.

The ACM were tested as potential adsorbents of phenols in an aqueous phase and this data is shown in Table 2. It can be seen that the monoliths of the honeycomb type series have a greater capacity for phenol retention compared to the disc type series. This is due to the fact that the honeycomb channels facilitate adsorption of this molecule since the problems of transport in solution are reduced. Figure 7 shows that when the surface area is larger, phenol adsorption increases. In addition there is a linear behavior to the data.

**Figure 7.** Phenol adsorption quantity as a function of the monolith area surface.

Scanning electron microscopy (SEM)

Microphotographs of the selected samples are shown in Figure 8. In both cases surface features and regions of internal and external structures can be seen, as can the empty spaces between the particles. They are comparable with those obtained in other similar works^{10, 15, 16} Figure 8a shows the drilling of the honeycombs and 8b the dimensions of small points of the structure of the discs.

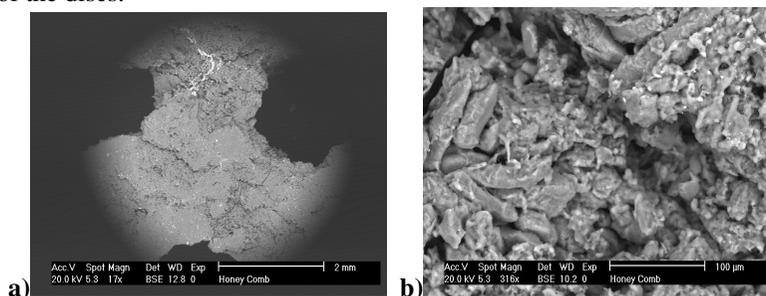


Figure 8. Microphotographs of SEM discs and honeycombs at 20%.

Conclusions

The use of ZnCl_2 as an impregnation agent is appropriate for activated carbon monolith synthesis. Using coconut shell as a precursor material resulted in structures that possessed good mechanical and textural properties. These properties were achieved due to the heating that takes place in the various processes of the preparation and the resulting structures could be used for the adsorption of different compounds.

The temperature formed by pressing of the precursor particles is key for the synthesis of the structures. The optimum temperature was found to be 423 K since at this temperature the loss of volatile matter is low, which helps with the resistance. Six samples of activated carbon monoliths (discs and honeycombs) were prepared, achieving BET areas between 702 and 1523 m^2g^{-1} , together with a microporous volume of between 0.38 and 0.79 cm^3g^{-1} . The most desirable characteristics were obtained in samples MFD132 (discs) and MFH232 (honeycombs), and were obtained under the same conditions, the shape of the structures being the only variation. Evaluation of the influence of the relationship between impregnation in an area and microporous volume found a maximum value in developing the area and micropores for a relation of 0.3 g of Zn per g of coconut. An increase in the yield from the carbonization process with a larger relative impregnation was also observed and attributed to a greater residual mass available for carbonization due to a larger amount of volatile matter retained, as illustrated by thermogravimetric analysis.

On comparison of the BET and Langmuir models, it was found that the V_m values were higher for the Langmuir model in all cases. Also, the immersion calorimetry in benzene showed a directly proportional relationship between BET area and enthalpy as a parameter characterization that demonstrates the solid-liquid interactions.

Finally, it was observed that the synthesized activated carbon monoliths are materials with potential application to the adsorption of phenol from aqueous solutions. Quantities of phenol adsorbed ranged between 7.38 and 35.91 $\text{mg}\cdot\text{g}^{-1}$ for phenol solutions of 500 mgL^{-1} and between 24.02 and 108.61 $\text{mg}\cdot\text{g}^{-1}$ for phenol solutions of 1500 mgL^{-1} , despite that the honeycombs retain a main quantity of phenol that discs similar areas, both were found to reduce the phenol concentration in a solution

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