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ADSORPTION STUDIES OF METHYLENE BLUE AND PHENOL ONTO PECAN AND CASTILE NUTSHELLS PREPARED BY CHEMICAL ACTIVATION

ESTUDIOS DE ADSORCIÓN DE AZUL DE METILENO Y FENOL EN NUECES DE PECAN Y DE CASTILLA PREPARADAS POR ACTIVACIÓN QUÍMICA

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Abstract

The use of agricultural wastes (AWs) as raw materials in the production of granular activated carbon (GAC) is an important topic worldwide. The abundance of pecan nutshells (PNs) and castile nutshells (CNs) provided the motivation for producing GAC from these materials. Phosphoric acid was used at several activation ratios (Rs), and the adsorption capacity of methylene blue (MB) and phenol (PH) by the products was measured. The highest GAC yields and the maximum adsorption capacities were obtained at R=2. Although the maximum MB adsorption capacity of GAC produced from CNs was relatively small, 170 mg g^{-1}; that of GAC produced from PNs was 400 mg g^{-1}, which is among the highest reported. The SEM images of GAC from PNs revealed an ordered arrangement of nearly straight and tubular macropores with abundant mesopores inside. The ball-pan hardness number of the PN GAC is 80, equal to the value reported for bituminous GAC. These characteristics make the GAC obtained from PNs suitable for packed tower applications.

Keywords: agricultural waste, granular activated carbon, activation ratio, pyrolysis.

Resumen

El uso de desechos de agricultura como materia prima en la producción de carbón activado granular (CAG) es un tema importante alrededor del mundo. La abundancia de cáscara de nuez de pecan (NP) y de castilla (NC) fue la motivación para la producción de CAG a partir de estos materiales. Se utilizó ácido fosfórico a distintas relaciones de activación (R) y se midió la capacidad de adsorción de azul de metileno (AM) y fenol. Los CAG con más altos rendimientos y mayores capacidades de adsorción se obtuvieron con R=2. A pesar de que la máxima capacidad de adsorción de AM del CAG producido con NC fue relativamente pequeña, 170 mg g-1; la del CAG producido con NP fue de 400 mg g-1, que se encuentra dentro de los valores reportados más altos. Las imágenes en SEM del CAG de NP revelaron un arreglo ordenado de macroporos tubulares y casi rectos con mesoporos abundantes dentro. La dureza según el método Ball-pan Hardness Number del CAG de NP es de 80, igual al valor reportado para el CAG bituminoso. Estas características hacen que el CAG obtenido de NP sea adecuado para su aplicación en torres empacadas.

Palabras clave: desechos de agricultura, carbón activado granulas, relación de activación, pirólisis.

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1 Introduction

Pecan and castile nutshells (PNs and CNs) are suitable raw materials for the production of granular and powder activated carbon because the nutshells are approximately 50% of the weight of the fruit. The nuts are commonly commercialized peeled, and the nutshells are retained at the packing site, making collection easy. In the State of Puebla, Mexico, alone, an estimated 442 tons of CNs and 1,768 tons of PNs were generated in 2007. Pecan nuts are an important crop internationally, and the US is the most important producer (with more than 100,000 tons produced per year), followed by Mexico. On the other hand, castile nuts are almost exclusively produced in the State of Puebla, Mexico, with an annual production of over 1,000 tons (USDA, 1997).

There are several types of agricultural by-products that have been used for granular activated carbon (GAC) production at laboratory or industrial levels. Coconut shells (Azevedo *et al.*, 2007), palm saw dust (Selvi *et al.*, 2001), moss (Subramani, 2002), oregano stems (Timur, 2002), sunflower seeds (Karagöz *et al.*, 2008), olive husks (Michailof *et al.*, 2008), corn husks (Tsai *et al.*, 2001), apple pulp (Suárez-García *et al.*, 2002), vetiver roots (Altenor *et al.*, 2009), grain sorghum (Yulu and Walawenderand, 2002), pistachio nutshells (Lua *et al.*, 2004), and wood (Heschel and Klose, 1995) are some examples. Even waste products such as activated sludge (Al-Qodah and Shawabkah, 2009) and turkey manure (Lima and Marshall, 2005) have been processed in an effort to produce GAC. The abundance of these resources in different places of the world can transform a by-product into a valuable raw material with potentially high profits. Bamboo in Malaysia (Hameed *et al.*, 2007), European cherry stones in Spain (Olivares-Marín *et al.*, 2007), and date stones in Saudi Arabia (Alhamed, 2006) are examples of low-cost, accessible raw material for the production of high quality activated carbon (AC). In addition to offering economic advantages over mineral or bituminous coal, agricultural waste (AW) can be processed at temperatures below 600°C, while ordinary coal yields its best results at over 800°C (Nowicki *et al.*, 2008).

The demand for GAC as a water-purifying agent has dramatically increased, as has its use in tertiary wastewater treatment. Color and odor removal are important in these processes. Other uses include fluids deodorization and color removal (Karim *et al.*, 2005), retention of toxic metallic substances (Srivastava, *et al.*, 2008; Jusoh *et al.*, 2007) retention of gold from gold bromine solutions (Pesic and Storhok, 1992), ventilation filters, solvent regeneration, and even catalyst support for liquid $HgCl_2$ (Kai *et al.*, 2009). The use of GAC columns in pre-treating water for desalination processes could minimize reverse osmosis costs by adsorbing suspended and soluble organic matter (Guy-Reznik *et al.*, 2008).

Experimentation and development of GAC from the AW mentioned above has been carried out using chemical activators such as KOH, $ZnCl_2$, H_2SO_4, H_3PO_4 and CO_2. Water vapor and other gases have also been used as physical activators. This treatment of the raw material before pyrolysis creates macropore, mesopores, and micropores on and inside the solid's surface. However, acid treatment improves the final quality of the GAC by introducing ions on the surface structure, such as chlorides, sulfates and phosphates (depending on the acid used), yielding a GAC capable of ion exchange (Cañizares *et al.*, 2006). It has been suggested that H_3PO_4 produces better modification to the botanic structure than other acids. These modifications are both physical and chemical and include penetrating, swelling, and partially dissolving the available biomass, dividing bonds and reforming new thermal resistant polymers (Girgis *et al.*, 2002; El-Qada *et al.*, 2008). This acid also acts as a stabilizer to prevent the collapse of the raw material, restricts the formation of tar and guarantees the creation of macropores that transport the fluid and mesopores and micropores to where the adsorption occurs (Ahmadpour *et al.*, 1998).

The quality of the GAC can be measured by superficial area, granulometry, dominant pore type, and adsorption indicators, among others. The factors that are most important in determining GAC quality are carbonization time, carbonization temperature and the activation ratio (R), which is the mass ratio of activator to raw material. The activator intervenes in the pyrolysis chemistry, mainly as a dehydrating agent. The activating ratio determines the product's porosity while the pyrolysis temperature determines the extent of the carbonization. Generally, a larger ratio of macropores to micropores is obtained from higher values of R

(Suárez-García *et al.*, 2002).

This work proposes the use of PNs and CNs as raw materials for the GAC production through activation with phosphoric acid to produce the best adsorption results. The effects of preparation conditions were studied on the final yield, and the adsorption capacity was measured through adsorption isotherms with methylene blue (MB) and phenol (PH).

2 Experimental procedures

2.1 Nutshell preparation

The nutshells were washed with tap water to eliminate any residue or foreign material and dried for 24 hours in a 110°C stove to eliminate humidity. The nutshells were partially crushed to facilitate handling in subsequent processing.

2.2 Impregnation and activation

The quantity of phosphoric acid (CAS 7664-38-2; Sigma-Aldrich 7664-38-2) determined by the R selected for each sample was dissolved in 25-mL of distilled water. This solution was mixed with clean, dry PNs or CNs in 250-mL covered flasks. These flasks were heated to 85°C and stirred at 150 rpm for 4 hours to increase acid penetration. After eliminating the excess liquid, the damp nutshell pieces were heated to 110°C for 24 hours to eliminate humidity.

2.3 Pyrolysis

The dried solids were introduced into porcelain crucibles and set in a furnace to carbonize at 500oC. The carbonization time was kept constant at 3 hours at maximum temperature for all tests, with heating and cooling ramps of 10°C/min. At the end of the pyrolysis process, the samples were cooled to 100°C and placed in a desiccator.

2.4 Washing and packing

The acid activator was completely removed from the GAC using distilled water. The samples were washed with boiling water, followed by cold water, until pH 6.0 was reached. The GAC was set to dry for 12 hours at 110°C and then packed in sealed bags for the following measurements.

2.5 Adsorption isotherm determination for MB (CAS 61-73-4; Sigma-Aldrich 7220-79-3) and PH (CAS 108-95-2; Sigma-Aldrich 108-95-2).

A total of 0.100 g of GAC in a 8-18 mesh range was weighed and mixed with different volumes (10, 12, 14, 16, 18, 20, 30, 40, and 50-mL) of a 1000 ppm MB solution in 250-mL flasks. For PH isotherms, 0.15 g of GAC in a 16-30 mesh range was weighed and mixed with different volumes (5, 20, 35, 65, 80, and 95-mL) of a 500 ppm PH solution. All flasks, at pH 7.0, were covered and left to stir at 125 rpm and 20oC for 72 hours. It was previously determined that after 48 hours dynamic equilibrium in the adsorption process was reached for the concentrations used. The remnant or equilibrium concentration, C_e, for each substance was determined with a UV/V (HACH DR/4000U) spectrophotometer. The amount adsorbed at equilibrium, q_e, was calculated through Eq. (1) from C_e, the initial concentration, C_o, the volume of solution, V, and the mass of carbon, m.

$$q_e = \frac{(C_0 - C_e)\,V}{m} \tag{1}$$

The absorbances were measured at the maximum absorption wavelengths, which were 265 nm for PH and 665 nm for MB. The compositions were transformed into the calibration lines given in Eqs. (2) and (3).

$$\text{Absorbance} = 0.0141[PH] \quad R^2 = 0.998 \tag{2}$$

$$\text{Absorbance} = 0.1682[MB] \quad R^2 = 0.994 \tag{3}$$

Langmuir's empirical model supported on kinetics was developed to describe adsorption onto activated carbon Eq. (4). The processes of adsorption and desorption are dynamic and a rate law can be written for each process, and when the rates become equal an equilibrium state will exist characterized by a constant fractional coverage of the original adsorption sites. Langmuir isotherm assumes homogenous adsorption with no transmigrations of the adsorbate in the surface.

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{4}$$

where q_e is the adsorption of the adsorbate per unit mass of the adsorbent at equilibrium in units of mg g^{-1}; K_L is the rate adsorption constant (ratio of adsorption over desorption rate constants) in units of L mg^{-1}; C_e is the solute concentration at equilibrium in units of mg L^{-1}; and q_{max} is the maximum solute adsorption capacity per unit mass of adsorbent in units of mg g^{-1}, and also the maximum adsorption site density.

Freundlich isotherm, Eq. (5), is the earliest known relationship describing the non-ideal and reversible adsorption, not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. Freundlich isotherm is widely used in heterogeneous systems for organic compounds in activated carbon.

$$q_e = K_F C_e^{1/n} \tag{5}$$

The value $1/n$ between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as it gets closer to zero. Whereas, a value below unity implies chemisorptions process where $1/n$ above one is an indicative of cooperative adsorption.

The experimental data were fitted to the original and the linear transformation of the Langmuir isotherms using Eqs. (4) and (6) and the original and linear transformation of Freundlich isotherms using Eqs. (5) and (7) to determine which of the two displayed the best goodness-of-fit value (R^2), and the adsorption constants were calculated from these isotherms. This is the conventional approach for modeling adsorption isotherm systems presented by Foo and Hameed (2010) in their review on the topic.

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \tag{6}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{7}$$

The essential characteristics of Langmuir isotherms were expressed in terms of the dimensionless separation factor, R_L, in Eq. (8), that includes Co, the maximum initial concentration, and the rate constant. This parameter indicates that adsorption is not favorable for $R_L > 1$, is linear for $R_L = 1$, favors GAC for $0 < R_L < 1$; and is irreversible for $R_L = 0$ (Karagöz *et al.*, 2008; Hameed *et al.*, 2007).

$$R_L = \frac{1}{1 + K_L C_0} \tag{8}$$

2.6 *Ball-pan hardness number (BPHN)*

The GAC sample with the highest q_{max} was tested to obtain its BPHN, also called the mechanical abrasion factor, according to D3802-79 ASTM standard and procedure with sieve numbers 8, 16 and 100 (ASTM Standards on Activated Carbon, 2006).

3 Results and discussion

3.1 *Pyrolysis yield*

The pyrolysis yield is defined as the mass of GAC obtained per mass of raw material. Table 1 shows the yields calculated at different activation ratios for PNs and CNs. In all cases, the original mass of the nutshells was 25 g. The yield increased at higher activation ratios and was higher for PNs, though the results did not follow a linear relationship. Yields above 50% are acceptable for GAC production and were obtained from both nutshells.

Table 1 Yields obtained at different impregnation ratios.

R	g GAC from CN	Y from CN, %	g GAC from PN	Y from PN, %
0.5	10.33	29.2	7.29	41.3
1	10.89	41.3	10.33	43.6
1.5	12.70	47.4	11.84	50.8
2	17.62	52.3	13.07	70.5

3.2 *Testing the adsorption isotherm models*

The experimental data obtained from the adsorption isotherm determination shows that both types of GAC lead to a Type I isotherm according to Brunauer classification, as it can be seen in Figs. 1 and 2.

These data were adjusted by linear transformation and are shown in Figs. 3 and 4. For these two samples, the best adjustment was obtained using the Langmuir model, Eq. (4). Adjustment to the Freundlich model, Eq. (5), was also tested.

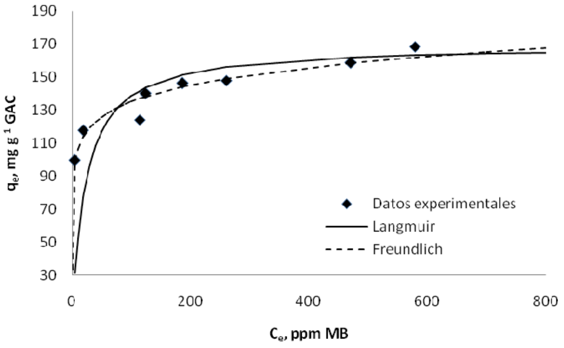

Fig. 1 Adsorption isotherms for MB on GAC prepared with R= 2 from CNs

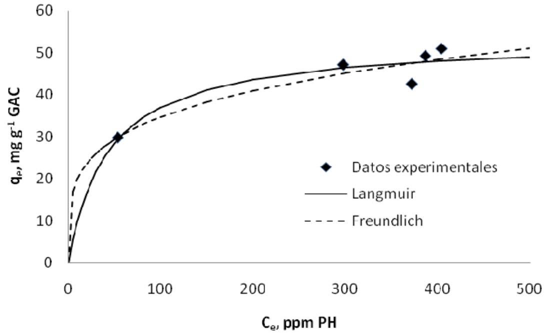

Fig. 2 Adsorption isotherm for PH on GAC prepared with R= 2 from CNs

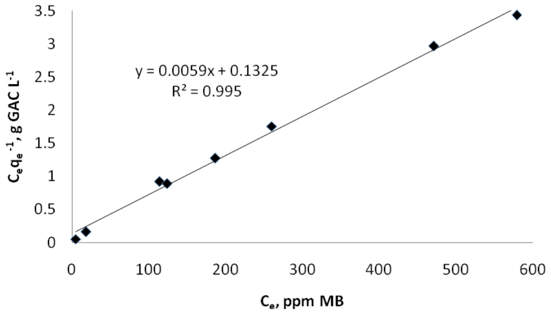

Fig. 3. Linear transformation of the adsorption isotherm for MB on GAC prepared with R= 2 from CNs using the Langmuir model.

The MB isotherms shown closely conform to Langmuir behavior for the entire range of tested concentrations. The adsorption data of MB on CN GAC prepared with $R = 2$ displayed a R^2 of 0.995 fitting with this model. In comparison, fitting to Freundlich's model yielded a R^2 of 0.937 and is shown in Fig. 5. A similar result was obtained with data from the other adsorption experiments.

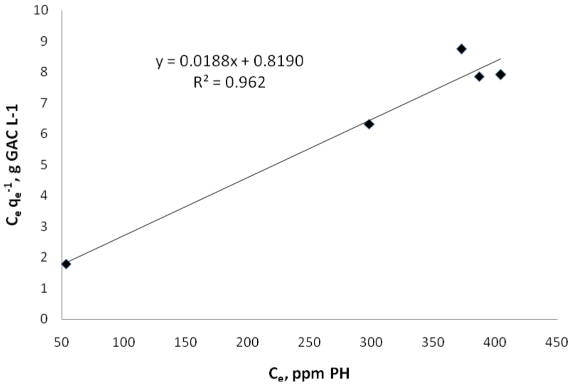

Fig. 4. Linear transformation of the adsorption isotherm for PH on GAC prepared with R= 2 from CNs using the Langmuir model.

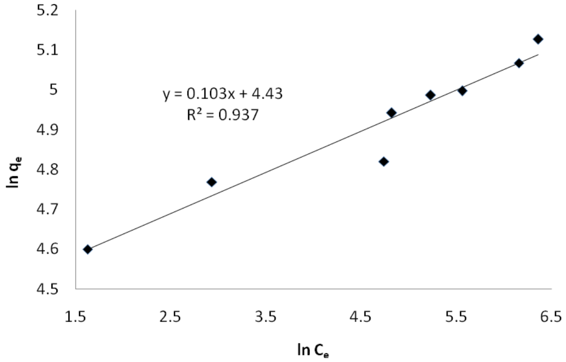

Fig. 5. Linear transformation of the adsorption isotherm for MB on GAC prepared with R= 2 from CNs using Freundlich's model.

The fact that Langmuir's isotherm model had a better adjustment indicates that this GAC will not abruptly desorb substrate molecules if the surrounding fluid concentration suddenly changes. The asymptotic nature of the Langmuir model gives stable adsorption at the maximum adsorptive capacity; therefore, it will perform better when used in industrial applications. Values of $K_L > 0$ in Table 2 confirm the type I isotherm favorable to adsorption.

An example of such an application is toxic metal removal and adsorption, in which the metal's concentration in the stream could change slightly, disturbing the GAC's mass transfer equilibrium. If the AC follows the Freundlich model, for example, with weaker molecular interactions between adsorbate and adsorbent, then the metal desorption could be prejudicial to the downstream process. However, if the AC follows the Langmuir model, this disturbancerelated desorption would be minimized, as it is shown with the low values of R_L in Table 2, which reflect that adsorption is more favorable (Foo and Hameed, 2010).

3.3 Effect of R on the GAC adsorption characteristics

Table 2 shows the results of the adsorption studies of GAC obtained with the Langmuir model from CNs and PNs. The comparison of GAC's based on adsorptive capacity is related to ASTM D 3860-98 "Determination of adsorptive capacity of activated carbon by aqueous phase isotherm technique" (ASTM Standards on Activated Carbon, 2006). This practice covers the determination of the adsorptive capacity of AC to remove undesirable constituents from wastewater as proposed in this work, particularly for the removal of color from dye mill and toxicants.

The GAC derived from PNs had better results than that from CNs for the activation ratios (Rs) tested for activating the carbon. The values of q_{max} for the MB of the GAC prepared from PNs are more than twice that of GAC prepared from CN with the same $R = 2$. The q_{max} for PH of the GAC prepared from PNs is three times that of GAC prepared from CNs at the same $R = 2$.

Table 2 also shows that all GACs produced presented a higher affinity towards MB than PH. This evidence indicates the presence of a greater quantity and density of macropores than mesopores or micropores and the capacity of the GAC for adsorbing molecules of similar molecular weight and size as MB.

Table 2. Adsorption parameters of Langmuir model for the adsorption of MB and PH on GAC produced from CN and PN.

Solute: MB	q_{max}	K_L	R_L	R^2
CN, R=2	169.5	0.045	0.022	0.995
CN, R=1	140.8	0.067	0.015	0.988
PN, R=2	400.0	0.625	0.004	0.999
PN, R=1.5	333.0	0.002	0.398	0.921
Solute: PH				
PN, R=1.5	103.1	0.005	0.289	0.933
PN; R=2	158.7	0.006	0.251	0.987
CN, R=2	53.2	0.023	0.080	0.962
CN, R=1.5	53.2	0.018	0.100	0.964

Table 3. Adsorption parameters of Freundlich model for the adsorption of MB and PH on GAC produced from CN and PN.

Solute: MB	K_f	n	R^2
CN, R=2	83.9	9.67	0.937
CN, R=1	91.2	15.60	0.860
PN, R=2	75.3	7.08	0.813
PN, R=1.5	3.14	1.66	0.978
Solute: PH			
PN, R=1.5	2.85	1.87	0.976
PN; R=2	5.99	2.01	0.978
CN, R=2	11.5	4.16	0.908
CN, R=1.5	9.25	3.65	0.890

The adsorption parameters obtained with the Freundlich model are shown in Table 3. The Langmuir model yielded a somewhat better fit than the Freundlich model. As also illustrated in Table 3, the values of $1/n$ are in between 0 and 1, which indicates favorable adsorption.

In Table 4, a comparison of the results obtained with GAC produced from other AWs shows that the GAC produced from PNs equals or surpasses the others. Also shows that the adsorption data for GAC produced from PNs with $R = 2$ had similar values of the adsorption parameters for the bamboo-based GAC. The capacity and strength of adsorption are similar and among the highest found in GAC from AW. The bamboo-based GAC had BET surface area, total pore volume and average pore diameter of 1896 m^2/g, 1.109 cm^3/g and 2.34 nm, respectively.

GAC from coconut shells is commercially available and used in several industrial applications in wastewater tertiary treatment, for example. The maximum monolayer adsorption capacity (mg g^{-1}) was determined as 277.90, below the value obtained for the PNs GAC (Kannan and Sundaram, 2001).

Table 5 shows the comparison with reported data for the adsorption of PH. The GAC from PNs had the highest q_{max} value and an intermediate value of R_L, implying both high adsorbate and reversible retention that make the GAC adequate for tertiary wastewater treatment.

3.4 SEM images of the PN and the GAC

The control sample is presented in Image 1. The surface of a PN without any thermal or chemical

Table 4. Langmuir constants for MB adsorption on GAC produced from different AWs.

Reference	(Thinakaran *et al.*, 2008)	(Hameed *et al.*, 2007)	(Timur, 2002)	This work
Raw material	Sunflower seed hull	Bamboo	Oregano stems	Pecan nutshells, R=2
q_{max} (mg g^{-1})	16.43	454.2	285.7	400.0
K_L (L mg^{-1})	1.15	0.518	0.686	0.625
R_L	0.050	0.004	0.005	0.004

Table 5. Langmuir constants for PH adsorption on GAC produced from different agricultural by-products.

Reference	Ramos-Rodríguez and Reyes-Mazzoco (2010)	Lam and Zakaria (2010)	Timur (2002)	This work
Raw material	Black cherry stones	Wood saw-dust	Oregano stems	Pecan nutshells, R=2
q_{max} (mg g^{-1})	133.33	149.25	94.34	158.7
K_L (L mg^{-1})	0.0086	0.160	0.010	0.006
R_L	0.47	0.04	0.51	0.251

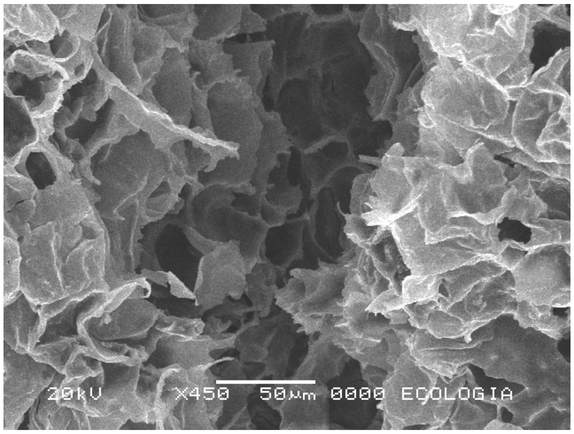

Image 1. Control sample of PN raw material. Scale line equals 50 μm.

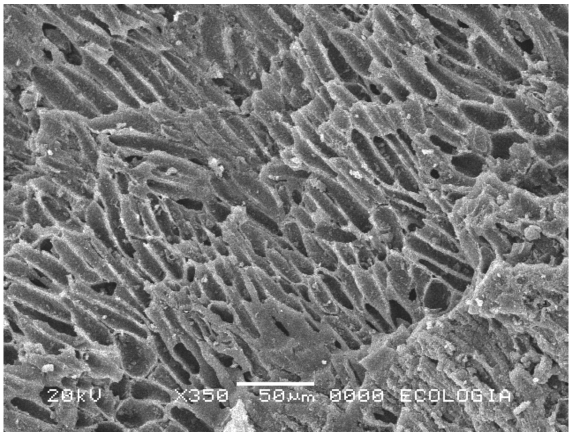

Image 2. GAC surface porosity. Scale line equals 50 μm.

modification is presented. Importantly, a concentration of pores appears on the PN surface. The solid is not entirely smooth but instead consists of crevices and pores of approximately 10 μm diameter.

When examining the SEM images of GAC produced at $R = 2$, porosity is observed at a scale of 10 μm, as shown in Image 2. These pores are responsible for reducing mass-transfer resistance for the adsorption (Gleisy *et al.*, 2008; Simpson, 2008). On the rough outer surface of the AC, 10 μm pores can be observed. This evidence confirms that this GAC sample contains a large amount of almost straight cylinders macropores. This GAC is recommended for adsorbing molecules of high molecular weight, such as multiple-ring molecules (> 128 amu), and molecules of intermediate weight, such as PH or single-ring organic molecules (78-128 amu).

The PN GAC sample in Image 3 shows a graphitic and structured porosity. Conduits of roughly 10 μm length with very small pores can be detected. The pores are aligned, and there is almost no space between pores, significantly incre-

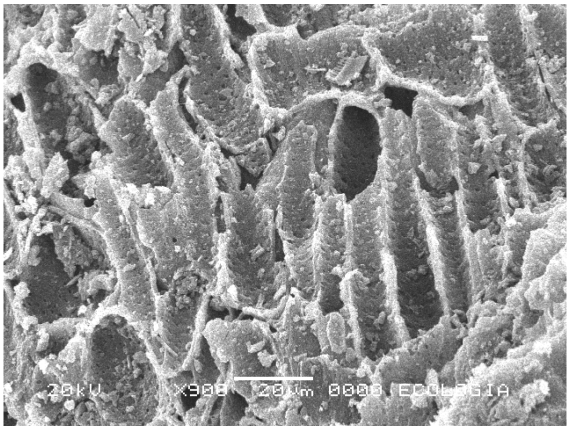

Image 3. Internal porosity of GAC produced from PN with R=2.

asing their density.

With the aid of these images and the adsorption isotherms, it is possible to understand the adsorptive behavior of GAC produced from PNs prepared under different conditions. GAC with a high maximum substrate adsorption and homogeneous surface trends has been manufactured, comparable with those produced from other agricultural waste products.

3.5 Ball-pan hardness number

The BPHN helps predict the lifespan of activated carbon in a packed tower, in which it may be susceptible to effects of abrasion, sheer stress and damage inflicted by surrounding fluids. GAC must have a high BPHN to withstand extensive usage and handling as well as regeneration processes and desorption, which also cause excessive vibrations. The BPHN for PN GAC samples was determined to be 80, equal to the BPHN of bituminous GAC and larger than that of lignite GAC that is 60 (Clark and Lynkins, 1991). This result makes the GAC produced from PNs suitable for packed tower applications.

Conclusions

Several activated carbons were produced from pecan and castile nutshells with highest total yields of 52% and 70%, respectively, with an impregnation factor of 2 g phosphoric acid per gram of raw material.

Adsorption isotherm results for methylene blue and phenol for the GAC samples best fit Langmuir's model. The adsorption capacities of MB and PH for GAC from pecan nutshells were among the highest for GAC produced from agricultural waste.

The pore structure observed through SEM images permitted greater adsorption of methylene blue because of the density of macropores and mesopores on the AC surface with strong bonding.

The BPHN of the pecan nutshell GAC was 80 making it suitable for applications in the removal of toxicants from water.

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