



## Adsorption studies of methylene blue and phenol onto black stone cherries prepared by chemical activation

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### ABSTRACT

The production of granular activated carbon (GAC) basically depends on the correct selection of carbonization temperature, activation ratio and agent (physical or chemical) as well as the raw material. Black cherry, available in Mexico with relative abundance, is of the same genus as the European cherry, whose stones have yielded good GAC production results. Black cherry stones were tried as raw material for GAC production with phosphoric acid as the activating agent. Optimum carbonization temperatures were found to be between 500 and 550 °C with an activation ratio of 1.0 g of phosphoric acid/g raw material. Under these conditions the maximum yield was 48.16 g of GAC/100 g black cherry stones. The experimental adsorption parameters fitted into Langmuir's model with a maximum adsorption of 321.75 mg of methylene blue/g GAC and 133.33 mg of phenol/g GAC. Black cherry shells are an abundant agricultural by-product with no uses, and therefore are an alternative for producing GAC.

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### 1. Introduction

There are several different types of agricultural by-products that have been used for activated carbon (AC) production at laboratory or at an industrial level. Coconut shells [1], palm saw-dust [2], moss [3], oregano stems [4], sun flower seeds [5], walnut shells, olives [6], corn husks [7], apple pulp [8], vetiver roots [9], sugar canes, grain sorghum [10], pistachio-nut shells [11] and wood [12] are some examples. Even waste products, such as activated sludge [13] and turkey manure [14] have been processed in an effort to produce AC.

All these materials offer an alternative to mineral or bituminous coal, the most demanded and typical raw material in AC production. In different areas of the world, the abundance of these resources can transform a by-product into a valuable raw material, with potentially high profits. For instance, bamboo in Malaysia [15], European Cherry (EC, *Prunus Virginiae*) stones in Spain [16] and date stones in Saudi Arabia [17] are examples of low cost accessible raw material for the production of high quality AC. Besides offering economic advantages over mineral or bituminous coal, agricultural wastes (AW) can be processed at temperatures below 600 °C, while ordinary coal yields its best results at over 800 °C [18].

Experimentation and development of AC based on the AW mentioned above has been carried out using chemical activators such as KOH, ZnCl<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> and CO<sub>2</sub>. Water vapor and other gases have also been used as physical activators. This treatment

on the raw material before its pyrolysis creates macro-, meso- and micropores on the solid's surface and also inside. Moreover, an acid treatment improves the final quality of the AC introducing ions on the surface structure such as chlorides, sulfates and phosphates depending on the acid used, yielding an AC capable of ion exchanging [19]. It has been suggested that phosphoric acid produces better modification than other acids both physically and chemically to the botanic structure by penetrating, swelling, and partially dissolving the available biomass, dividing bonds and reforming new thermal resistant polymers [20].

On the other hand, it has been shown that by using potassium salts to produce alkaline hydrolysis on the organic material it is possible to produce AC with superficial areas from moderate to high with substantial porosity. However, this requires considerably more water for washing and rinsing by unit mass, in comparison with acid activation. This is due to the difficulty of eliminating potassium salts located in the entire porous structure [21]. A similar result produces ZnCl<sub>2</sub> as an activator.

The quality of granular activated carbon (GAC) can be measured quantifying factors such as superficial area, granulometry, dominant pore type, and adsorption indicators among others. The factors that have the most important effect on GAC quality are carbonization time (ct), carbonization temperature (cT) and the activation ratio, which is the mass ratio of activator/raw material (R). 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, the higher the R, the greater the ratio of macropores to micropores is obtained [8].

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Uses and applications for AC include deodorizing and decolorizing of fluids [22], recovering precious metals [23] or metallic complexes, ventilation filters, solvent regeneration and even catalyst support for liquid  $\text{HgCl}_2$  [24]. The demand for AC as a water-purifying agent has dramatically increased. Its use in pre-treating water in desalination processes could minimize inverse osmosis costs by adsorbing suspended and soluble organic matter [25].

The retention of toxic metallic substances has been accomplished through adsorption on GAC [26,27]. Similarly, the adsorption of metal ions like Cu(II), Pb(II), Cr(III) and Cd(II) onto Turkish kaolinite clay [28], expanded perlite [29], Celtek clay [30], or colemanite ore waste [31] has also proven a consistent solution for the removal of heavy metals.

This work proposes the use of black cherry (*Prunus Serotina*) stones (BCS), as raw material for the production of a GAC, which could give as good results as the product obtained from EC stones [16] that come from trees of the same genus. The activation with phosphoric acid was selected because of its wide use as an activator and because it yields the best adsorption results among acid activators [20]. Effects of preparation conditions were studied on the final yield and adsorption capacity measured through adsorption isotherms with methylene blue (MB) and phenol (PH).

## 2. Experimental procedures

### 2.1. BCS preparation

The whole fruit was stripped of its pulp (main ingredient for jam preparation) to expose its rigid center or stone. The stone was opened, and the inner seed removed (another edible by-product). The two stone halves were washed with tap water to eliminate any residue or strange material, and dried for 12 h in a 105 °C stove to eliminate humidity.

### 2.2. Impregnation and activation

The quantity of phosphoric acid (CAS 7664-38-2; Sigma–Aldrich 7664-38-2) determined by the impregnation ratio ( $R$ ) selected for each sample, was dissolved in 25 mL of distilled water. This solution was mixed with clean and dry BCS in 250 mL covered flasks. These flasks were heated to 85 °C and stirred at 150 rpm for 4 h to increase the acid penetration. After eliminating the excess liquid, the heterogeneous mixture was heated to 110 °C for 12 h to eliminate humidity.

### 2.3. Pyrolysis

The dried solids were introduced into porcelain crucibles and set in a furnace to carbonize at different temperatures ( $cT$ ). The carbonization time was kept constant at 3 h at maximum temperature, with heating and cooling ramps of 10 °C/min. At the end of the pyrolysis process, when samples cooled to 100 °C, these were placed in a desiccator.

### 2.4. Washing and packing

The acid activator was completely removed from the GAC using distilled water. It was initially washed with boiling water and then with cold water until pH 5–6 was reached. The GAC was set to dry for 12 h at 110 °C.

### 2.5. Experimental designs

The yield for GAC production was altered manipulating the variables  $cT$  and  $R$ . Two experimental factorial, non-replicated

**Table 1**  
Pyrolysis yield.

$T^\circ\text{C}/R$	1	3	5
550	53%	45%	45%
700	20%	4%	5%
850	2%	0%	0%

matrixes were constructed with the values of these factors at three levels.

2.6. 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 the range 8–18 mesh was weighed and mixed with different volumes of MB (1000 ppm) in 250 flasks. For PH isotherms, 0.015 g of GAC in a 16–30 mesh range was weighed. These samples were mixed with different volumes of a 500 ppm PH solution. All flasks were covered and left to stir at 150 rpm for 72 h. It was determined, that after this time, dynamic equilibrium in the adsorption process was reached. The remnant concentration for each substance was determined with a UV/V (HACH, DR/4000U) spectrophotometer.

The absorbances at the maximum absorption wavelength were measured (270 nm for PH and 660 nm for MB). The data for the solutions prepared in several different compositions were transformed into calibration lines, Eqs. (1) and (2):

$$\text{Absorbance} = 0.181 [\text{PH}] \quad R^2 = 0.991 \quad (1)$$

$$\text{Absorbance} = 0.015 [\text{MB}] \quad R^2 = 0.998 \quad (2)$$

The experimental data was fitted to the linear transformation of Langmuir and Freundlich isotherms to find out which one displayed the best fit value, and thus calculating the maximum substrate adsorption ( $q_{\text{max}}$ ).

### 2.7. Mechanical abrasion factor

The GAC samples with the highest  $q_{\text{max}}$  were tested to obtain their mechanical abrasion factor according to D3802-79 ASTM standard and procedure with sieves numbers 8, 16 and 100 [32].

## 3. Results and discussion

### 3.1. Pyrolysis yield

The experimentation was centered on the variables that presented the most significant effect on the GAC production:  $cT$ , and  $R$  [8,20]. Other variables such as carbonization time, activator, and heating velocity were kept constant. In the experimental designs, the pyrolysis tests were randomized to reduce experimental error [33]. This allows a proper analysis of the variance of the experimental pyrolysis results.

The first experimental un-replicated design was constructed to determine the effect of  $cT$  and  $R$  on the GAC's final yield. Experiments were conducted at 550, 700 and 850 °C at an impregnation ratio of 1, 3 and 5. This exploratory design was based on a wide variable range to obtain the trend, which had the purpose of designing further experiments that could study the best conditions for GAC production. The results for GAC final yield expressed as percentage of the original mass are presented in Table 1.

In Table 1 it is possible to note that the yield drops dramatically when  $cT$  rises above 550 °C. The increase in  $R$  above unity reduced the yield, but the effect of this variable is not as significant as the effect of temperature. Table 2 was proposed to explore  $cT$  and  $R$

**Table 2**  
Pyrolysis yield.

T °C/R	0.5	1	1.5
500	53%	48%	45%
550	52%	46%	42%
600	36%	33%	32%

effects in narrower intervals with the consequent reduction in the variation of yield results.

The analysis of variance (ANOVA) carried out with the software Design Expert 6.0.6 of this factorial model with the original values of the two variables provided the best fit for a quadratic model, Eq. (3):

$$\text{Yield} = -463.12 + 2.08 \times cT - 34.06 \times R - 2.06E - 3 \times cT^2 + 2.53 \times R^2 + 0.04 \times cT \times R \quad (3)$$

Table 3 presents the ANOVA results for the experimental design that studied the total GAC yield. The quadratic model displays a non-linear relationship between cT and R on the yield. The most significant variable was cT, with mean square values for the linear and quadratic terms over three times those of R. Also, inserting the values of the variables in Eq. (3) it is possible to verify that the linear term for cT defines the value of the yield. Additionally, the mean square values for the lack of fit and error are low enough to state that the experimentation was carried out properly.

The effect of cT on yield was non-linear, with no major loss when moving from 500 to 550 °C but dropping considerably when cT increased above 600 °C. Therefore, the GAC samples with R=1 and cT=550 and 500 °C were selected for adsorption testing, and further characterization.

### 3.2. GAC characterization

Linear transformations of the adsorption isotherms for GAC samples are shown in Figs. 1 and 2 with the best adjustment to the Langmuir model, Eq. (4). The adjustment to the Freundlich model, Eq. (5) was also tested but produced a lower value of R<sup>2</sup> (goodness of fit):

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad (4)$$

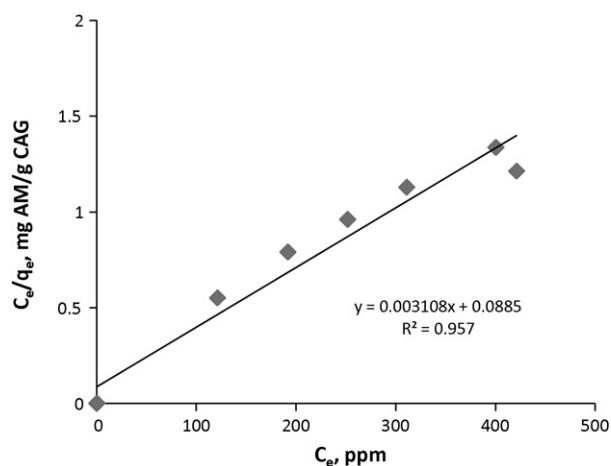
$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

where  $q_e$  = adsorption at equilibrium (mg solute/g solid);  $K_L$  = equilibrium adsorption constant (L/mg solute);  $C_e$  = solute concentration at equilibrium (mg solute/L);  $q_{\max}$  = maximum adsorption capacity (mg solute/g solid);  $K_F$  = Freundlich adsorption constant (L<sup>1/n</sup> mg solute<sup>n</sup>/g solid).

The MB isotherm shown in Fig. 1, closely conforms to the Langmuir model behavior until reaching a remnant ( $C_e$ ) concentration

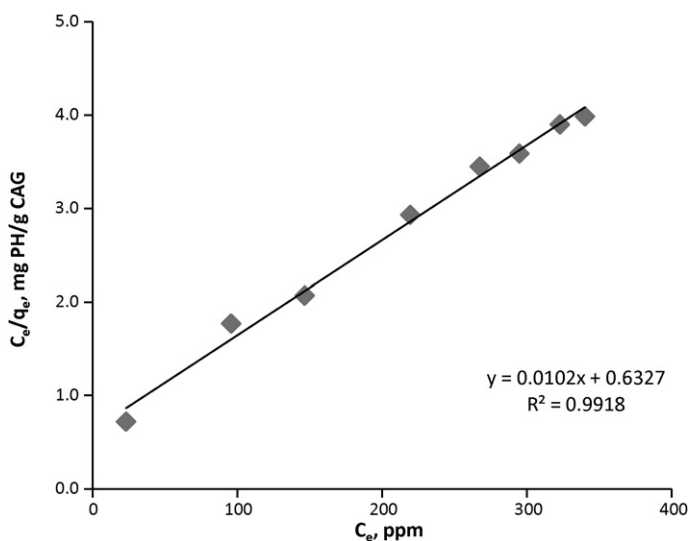
**Table 3**  
ANOVA for BCS yield of activated carbon for the experimental design for GAC yield.

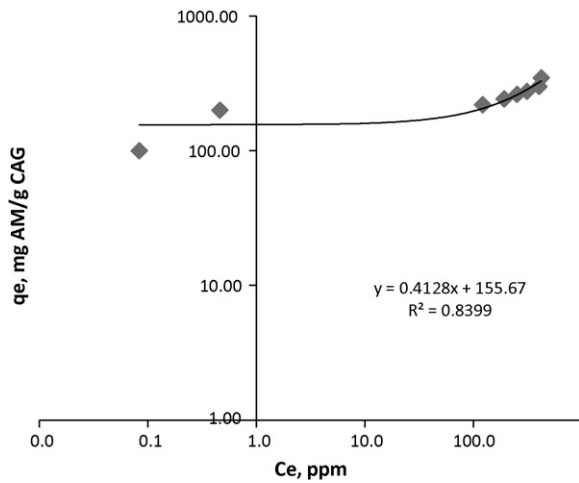
Source	Sum of squares	DF	Mean square	F value	Prob. > F
Model	509.52	5	101.9	178.39	<0.0001
Ct	334.95	1	334.95	586.35	<0.0001
R	91.96	1	91.96	160.99	<0.0001
cT <sup>2</sup>	73.19	1	73.19	128.12	<0.0001
R <sup>2</sup>	1.1	1	1.1	1.93	0.2071
cT × R	3.71	1	3.71	6.49	0.0383
Residual	4	7	0.57	–	–
Lack of fitness	3.78	3	1.26	22.68	0.0057
Error	0.22	4	0.06	–	–
Cor. total	513.52	12	–	–	–

**Fig. 1.** Linear transformation of the adsorption Isotherm for MB (cT=550 °C, R=1) to Langmuir's model.

of 400 ppm. For higher concentration values, linearity is no longer kept and the behavior of those concentrations deviates from linearity, because of the assumption in Langmuir's model of a monolayer of adsorbate on the GAC's surface.

The adsorption data of MB and PH displayed a R<sup>2</sup> of 0.957 and 0.991 fitting to Langmuir's adsorption model; in comparison to Freundlich's model, which yielded a R<sup>2</sup> of 0.84 as shown in Fig. 3. The fact that Langmuir's had a better adjustment indicates that this GAC will not desorb substrate molecules abruptly if the surrounding fluid concentration suddenly changes. The asymptotic nature of the Langmuir model provides a stable adsorption when reaching its maximum adsorptive capacity; hence, will have a better performance when used in industrial applications. An example is toxic metal removal and adsorption, where the metal's concentration in the stream could change slightly representing a disturbance to the GAC's mass transfer equilibrium. If the AC follows a Freundlich model for example, with weaker molecular interactions between adsorbate and adsorbant, then the metal desorption could be prejudicial to the downstream process, whereas if the AC follows the Langmuir model, this disturbance-related desorption would be minimized.

**Fig. 2.** Linear transformation of the adsorption isotherm for PH (cT=550 °C, R=1) to Langmuir's model.



**Fig. 3.** Linear transformation of the adsorption isotherm for MB ( $cT = 550\text{ }^\circ\text{C}$ ,  $R = 1$ ) to Freundlich's model.

Langmuir adsorption isotherm of the GAC produced at  $cT = 500\text{ }^\circ\text{C}$  for MB is displayed in Eq. (6) and for PH in Eq. (7):

$$\frac{C_e}{q_e} = 0.0033C_e + 0.076 \quad R^2 = 0.09 \quad (6)$$

$$\frac{C_e}{q_e} = 0.0075C_e + 0.87 \quad R^2 = 0.99 \quad (7)$$

Table 4 shows that carbon produced at  $500\text{ }^\circ\text{C}$  presented a slightly higher affinity towards PH, rather than to MB. This evidence suggests that the GAC porous structure had mainly micro- and mesopores that have a preference for medium size molecules, such as aromatic compounds. GAC prepared at  $550\text{ }^\circ\text{C}$  displayed the best MB adsorption, indicating the presence of a greater quantity and density of macropores and the capacity of GAC for adsorbing molecules of similar molecular weight and size as MB.

Table 5 shows the adsorption data for GAC produced from BCS compared with data from other agricultural wastes. PH adsorption displayed a  $q_{max}$  of  $133.33\text{ mg phenol/g GAC}$ , that is superior to Castile nut shells, and oregano stems.

Table 6 has the constants for Langmuir adsorption for MB on the GAC produced at  $cT = 550\text{ }^\circ\text{C}$ , compared to those obtained by other authors on AC produced from agricultural wastes. MB adsorption in this work is highly superior to that achieved by sunflower seeds and oregano stems; only the GAC produced from bamboo presented a higher MB adsorption capacity.

**Table 4**  
GAC maximum adsorption produced under  $R = 1$ .

$cT\text{ (}^\circ\text{C)}$	$q_{max}$	
	MB	PH
500	298.15	133.33
550	321.75	98.04

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

By-product Material	Black cherry stones	Nut shells [34]		Wood saw-dust [12]	Oregano stems [4]
		Castile	Pecan		
$q_{max}$	133.33	53.19	200.00	149.25	94.34
$q_{max}K_L$	1.148	1.22	0.70	23.88	0.94
$K_L$	0.0086	0.023	0.004	0.160	0.010

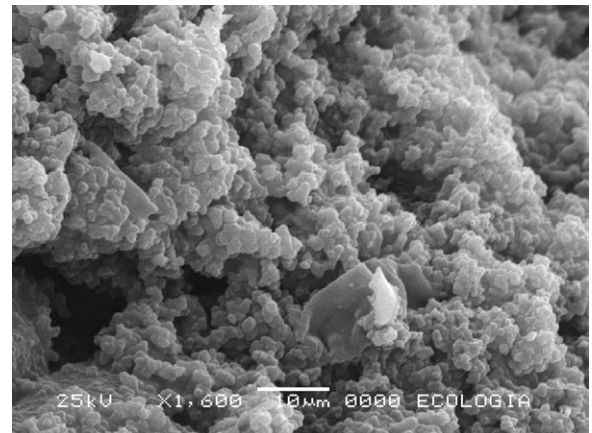
**Table 6**  
Langmuir adsorption comparison for MB on GAC produced from different waste materials.

By-product	Black cherry stones $cT = 550\text{ }^\circ\text{C}$	Sunflower seeds [5]	Bamboo wood [15]	Oregano stems [4]
$q_{max}$	321.75	16.43	454.20	285.70
$q_{max}K_L$	11.299	0.378	1.590	45.712
$K_L$	0.0351	0.023	0.004	0.160

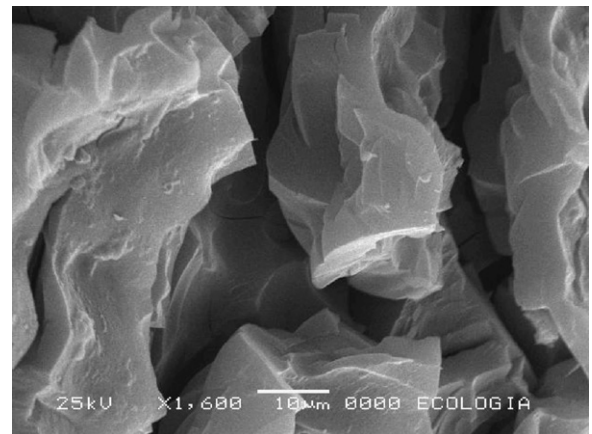
### 3.3. SEM images of the GAC

When examining SEM images of the GAC produced at  $cT = 500\text{ }^\circ\text{C}$  and  $R = 1$  (Image 1), important porosity is observed at a scale of  $10\text{ }\mu\text{m}$ . These pores are suggested to be responsible for the adsorption [35,36]. At the rough outer surface of the GAC,  $10\text{ }\mu\text{m}$  pores can be visualized and even narrower conducts. This evidence confirms that this GAC sample presents predominantly mesopores. Such GAC is recommended for adsorbing molecules of high molecular weight, such as multiple-ring molecules ( $>128\text{ amu}$ ) and also medium or intermediate weight ones, such as PH or single-ring organic molecules ( $78\text{--}128\text{ amu}$ ).

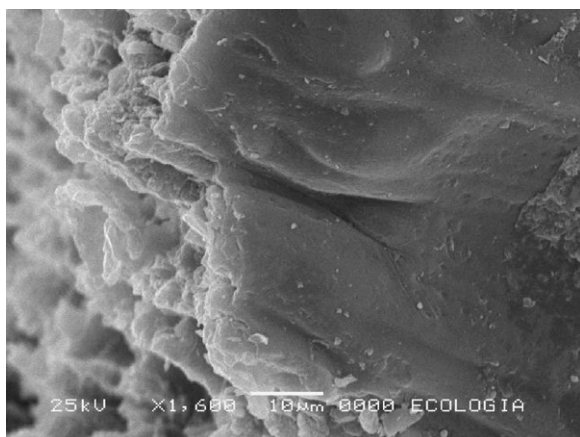
A GAC sample produced at  $cT = 550\text{ }^\circ\text{C}$  is shown in figure (Image 2). Important changes are verified on the solid's surface when increasing only  $50\text{ }^\circ\text{C}$ . The pores and the rough structure formed at  $500\text{ }^\circ\text{C}$ , have now changed into pores that are broader and different in shape, resulting in a completely different surface image. This figure shows a graphitic structure of random porosity. Conducts with pores greater than  $10\text{ }\mu\text{m}$  can be observed. Furthermore,



**Image 1.** GAC porosity ( $cT = 500\text{ }^\circ\text{C}$ ,  $R = 1$ ).



**Image 2.** Surface and porosity of GAC produces at  $cT = 550\text{ }^\circ\text{C}$  and  $R = 1$ .



**Image 3.** Control sample of BCS.

a greater space between pores can be seen, significantly reducing their density by surface area.

The control sample is presented in *Image 3*. The surface of the black cherry stone without undergoing any thermal or chemical modification is presented. An important concentration of tiny pores appears on the BCS surface. The solid is not entirely smooth, but instead consists of holes and pores up to approximately 20  $\mu\text{m}$  in diameter with inner cylindrical pores 5–1  $\mu\text{m}$  in diameter.

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

#### 3.4. Mechanic abrasion number

The abrasion number helps foresee the lifespan of activated carbon in a packed tower, wherever it may be susceptible to effects of abrasion, shear stress and damage inflicted by surrounding fluids. GAC must have a high abrasion number to withstand extensive usage and handling as much as possible; as well as regeneration processes and desorption or even excessive vibrations [37].

The abrasion number for GAC samples was determined to be 0.86 for  $cT = 500^\circ\text{C}$ , and 0.60 for  $cT = 550^\circ\text{C}$ , that are comparable to those obtained with bituminous AC (0.8) and lignite AC (0.6) [37]. These numbers also show that the mechanic resistance of GAC is proportional to the thermal degradation experienced during production. An extra  $50^\circ\text{C}$  during the pyrolysis of the GAC caused the loss of 30% of the mechanic resistance.

## 4. Conclusions

Two samples of activated carbon were produced from black cherry stones (*Prunus Serotina*) showing a high total yield of 48%, an abrasion number as high as 0.86 and acceptable adsorption parameters for MB and PH seen as adsorption capacity.

The temperature and activation ratio tested produced two GAC with different properties. The pore structure permitted the preferential adsorption of phenol or methylene blue. The maximum adsorption capacity was as high as the one found in other studies for the preparation of GAC from agricultural wastes.

Adsorption isotherm results for methylene blue and phenol for both GAC samples had their best fit in Langmuir's model. Methylene blue adsorption suggested a predominant density of macro- and mesopores on the AC surface. The increase in pyrolysis temperature suggests an increase in macropore density.

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