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Influence of Pretreatment with Soda (NaOH) on the Structural Characteristics of Activated Carbon Prepared by Chemical Means with H_3PO_4 from Rice Bran

Clément K. Balogoun[1], Ibrahim Tchakala[2], Mike Medokponou[3], Moctar L. Bawa[2], Dominique C. Sohounhloue[1], *

[1]Applied Chemistry Study and Research Laboratory, Polytechnic School of Abomey-Calavi University, Abomey-Calavi, Benin

[2]Water Chemistry Laboratory, Faculty of Science, University of Lomé, Lomé, Togo

[3]Water Science and Technology Laboratory, Polytechnic School of Abomey-Calavi University, Abomey-Calavi, Benin

E mail address:

csohoun@gmail.com (D. C. Sohounhloue)

*Corresponding author

Abstract: The purpose of this work is the preparation of best activated carbons from rice bran through carbonization at 500°C preceded by an impregnation in a 25% H_3PO_4 solution. We carry out the study of the effects of pretreatment with soda and Xp impregnation ratio on characteristics of three series of activated carbons SR_{0N}, SR_{1N} and SR_{2N} corresponding to the pre-treatment with soda 0 M, 1 M and 2 M respectively. The iodine value and the textural properties of prepared carbons have been determined. The maximum iodine value, 893 mg.g^{-1} is obtained in the SR_{2N} series for Xp = 2.5. In the SR_{1N} series the maximum iodine value 866 mg.g^{-1} is obtained for Xp = 4. Also activated carbons CS_1 (SR_{1N} - Xp = 4) and CS_2 (SR_{2N} - Xp = 2.5) have the following characteristics: specific surface area equal to 1711.6 and 1558.5 m^{2}g^{-1} and porous volumes of 1.234 and 1.385 cm^3/g respectively. Studies conducted on phenol adsorption and thermodynamic showed that CS_1 is slightly more effective than CS_2 with a spontaneous and exothermic reaction. On the other hand, their adsorption isotherms are best described by the Langmuir model than that of Freundlich.

Keywords: Rice Bran, Activated Carbon, Chemical Activation, Impregnation Ratio, Adsorption Isotherm

1. Introduction

Activated carbon is one of the most used adsorbent due to its large surface area [1, 2], favorable distribution of the pore size and the high degree of responsiveness of its surface area [1, 2]. In recent decades, adsorption systems involving activated carbon in chemical engineering, food and pharmaceutical industries have become important [2]. Activated carbon precursors generally come from two sources: fossil (lignite, peat and coal) and plant material [3]. Plants: particularly agricultural residues which are renewable and low cost precursors. So, some of them are used for the production of activated carbons. They are mainly: the bark and wood [4, 5], coconut shells [6, 7], almond shell [8, 9], pecan shells [10], pistachio nutshells [11], olive kernels [12], date stones [13, 14], apricots kernels [15] cherry stones [16], rice bran [17, 18], etc. One of the main agricultural sectors which generate large quantities of residues in Benin is rice. Indeed, from 2008 to 2013, the production of rice in Benin rose from 112705 tonnes to 206943 tonnes [19]. Benin has two rice mills including one at Glazoué in the central part of the country and the other at Malanville in the North. Two types of residues come from the production of rice. They are bran and straw. Straw is often burned on site or used as domestic energy for cooking. Bran is used as feed additive in livestock production and industry. These two residues can be valued also for the production of activated carbons. Rice bran represents approximately 20% of the total weight of the paddy [20].

In this study, we decide to develop activated carbon from rice bran through chemical way with phosphoric acid. Chemical activation is preceded by pretreatment with soda at various concentrations. As chemical activation, H_3PO_4 is widely used in the preparation of activated carbons from lignocelluloses products and offer certain advantages such as: its less polluting nature compared to zinc chloride $ZnCl_2$ and ease of its elimination by extraction with water [21].

Activation with phosphoric acid directly from rice bran gives a low specific surface area activated carbon [22]. This is due to the high content in ash (15.05% in mass) of rice bran [23]. This ash made up more than 96% of silica [23], can be eliminated by a leaching process at the base [24]. Previous work for the preparation of activated carbon from rice bran did not assess the effect of the concentration of the soda solution used for the pretreatment before the chemical activation with phosphoric acid, on the texture of the prepared activated carbon.

The objective of this work is to obtain an activated carbon with a large surface area for adsorption, an important porous volume and can adsorb a variety of pollutants contained in water. The work is to act on the concentration of the soda solution during pretreatment, and the impregnation ratio of the phosphoric acid solution during the activation by following the evolution of the iodine value, of the BET surface and porosity. The study of the effectiveness of the CS_1 and CS_2 activated carbons is conducted from the phenol adsorption. Adsorption isotherms are studied and different models are used to explain the possible adsorption mechanism.

2. Materials and Methods

2.1. Materials and Preparation Methods

2.1.1. Materials

Rice bran comes from the Glazoué mill, located in the central part of Benin republic. It was thoroughly washed with distilled water to remove impurities, and then dried at 110°C in the Heraeus INSTRUMENT oven for 24 hours. The resulting raw material served in the preparation of three series of activated carbons (SR_{0N}; SR_{1N} and SR_{2N}).

2.1.2. Preparation Methods

The process consists of three steps. The first step is to soak 10 g of rice bran in 80 ml of each of the NaOH soda solutions (0 M, 1 M and 2 M) to obtain AC, SR_{0N}, SR_{1N} and SR_{2N} respectively. The completed mixture is then dried at 110°C in the oven for 24 h and washed several times until the constant pH, then dried again in the oven at 110°C for 24 h. The second step is to soak the rice bran in a solution of phosphoric acid of 25% concentration (Vacide/Vsolution) for Xp impregnation ratios ranging between 1.5 and 4 grams of acid per gram of rice bran and then heat the mixture to reflux at 100°C for 2 h. Thus soaked rice bran is dried in an oven at 110°C. The last step is to carbonize the obtained carbon in a furnace (Nabertherm LE14 C290/11) at 500°C for 2 h in an inert to liquid nitrogen atmosphere. After cooling to ambient temperature in a dryer, activated carbon is washed first with a 0.1 M hydrochloric acid solution then rinsed several times with distilled water until the constant pH.

2.2. Characterizations

2.2.1. Yield of Activated Carbons

The yield of the prepared activated carbon was estimated from the following equation:

$$\text{Yield of Activated Carbon (wt \%)} = \frac{\text{mass of activated carbon}}{\text{mass of rice bran}} \times 100 \ (1)$$

2.2.2. Iodine Value of Activated Carbons

Iodine value is the classic test used to determine the adsorption capacity of activated carbon. Iodine value of prepared activated carbons was determined using ASTM standard D4607-94, (2006) [25]. The quantity of iodine adsorbed (in mg) per gram of activated carbon with a residual concentration of iodine of 0.01 M, represents the iodine value, ASTM D4607-94, (2006) [25].

To determine the iodine value we proceed as follows:

a. 50 ml of 0.05 M iodine solution is added to three different masses of samples of activated carbon contained in three Erlenmeyer flask of 250-ml, initially wet with 5 ml of HCl at 5%;

b. the contents of the flask is shaken vigorously for 30 (± 1) seconds and then quickly filtered through a pleated filter paper Whatman, No. 2V.

c. 25 ml of the filtrate is titrated with a solution of 0.1 M sodium thiosulfate until the solution becomes pale yellow. 2 ml of a solution of starch indicator (1 g/L) have been added, and the dosage was pursued with sodium thiosulfate until the solution becomes colorless. You notice V_2, the volume of consumed thiosulfate.

d. the quantity of adsorbed iodine is determined in mg per gram of activated carbon for each of the three masses, that is X/m_{CA}

$$\frac{X}{m_{CA}} = \frac{126,9044}{m_{CA}}(100.C_1 - 110.C_r) \qquad (2)$$

with $C_r = \frac{C_2 V_2}{V}$

Where C_r is the concentration (M) in residual iodine of the filtrate, C_1 the molarity of the iodine solution; C_2, the molarity of the thiosulfate solution and V the volume of titrated filtrate (V = 25 ml).

To determine the iodine value, you plot as a graph X/m_{CA} = f(C_r) using the three masses. This graph is a straight line. Iodine value corresponds to the value X/m_{CA} for which residual iodine concentration is 0.01 M.

2.2.3. Textural Characterization: Specific Surface Area and Porous Structure

The texture of activated carbons was determined by nitrogen adsorption N_2 at 77 K. This measurement was made with the multi gas ASAP 2020 M porosimeter. The specific surface area (S_{BET}) was determined by using the equation of Brunauer, Emmett and Teller (B.E.T). The total porous volume V_T, was defined as the volume of liquid nitrogen corresponding to the quantity adsorbed at the highest p/p_0

relative pressure = 0.99 [26]. The microporous Vμ volume, was determined by the micro pores (MP) analysis method. The volume of mesopores (V_{meso}) was determined by the method of Barrett, Joyner and Halenda BJH. The microporous volume, Vμ, was determined by the t-plot method proposed by Harkins and Jura. For mesopores volume (V_{meso}), the Barrett Joyner and Halenda BJH method was used for its calculation. The average diameter of the pores Dp, was calculated from the relationship $4V_T/S_{BET}$, and DTP pores size distribution was appreciated by using the BJH model, and that of Horvath-Kawazoe.

2.2.4. Chemical Characteristics

Chemical characteristics (chemical functions of surface areas, pH zero point of charge) of prepared activated carbons were determined from the methods of Boehm, (1994) [27] and Noh and Schwarz, (1989) [28], respectively. The method of Boehm is one of the techniques most commonly used to quantify and differentiate between groups of surface on activated carbons of different acid strength [29, 30].

2.3. Phenol Adsorption Isotherms

Phenol adsorption capacities (C_0 = 20 mg.L^{-1}) on activated carbons CS_1 and CS_2 have been evaluated by the isotherms study.

2.3.1. Batch Adsorption Experimental Device

Experiments of phenol adsorption by the activated carbons CS_1 and CS_2 were conducted in "batch method" (in simple 125 ml Erlenmeyer flasks), at ambient temperature (27 ± 2°C) and at a shaking speed of 150 rpm. Chemical equilibrium is reached at the end of 3 h. After this equilibration time solutions are filtered using a filter paper (Whatman No. 2V) to determine the residual concentration. The maximum adsorption capacity at equilibrium (mg/g) of each dye was calculated using the relationship:

$$q_e = \frac{(C_i - C_e) \cdot V}{m} \qquad (3)$$

Where C_i and C_e (mg/L) represent the initial concentration and the adsorbate equilibrium respectively, V the volume of the solution and m the mass of dry activated carbon used.

2.3.2. Determination of Phenol

The phenol concentration is determined using the standard method APHA [31]. The principle of this method is based on the condensation in a basic environment between the phenolate ion and the 4-amino antipyrine in the presence of an oxidant, potassium hexacyanoferrate (III) (potassium ferricyanide). The absorbance of the sample is measured at 510 nm, using a Hach-Lange 5000 DR spectrophotometer.

2.4. Thermodynamic Study of Phenol Adsorption on Activated Carbons CS_1 and CS_2

The influence of temperature on adsorption is associated with several thermodynamic parameters. The determination of these thermodynamic parameters is necessary to determine whether the process is spontaneous or not. These parameters that are: the variation of Gibbs free energy ΔG^0, the variation in enthalpy ΔH^0 and the variation of entropy ΔS^0 can be determined from the equilibrium constant K_e for different temperatures [32]. The variation of Gibbs free energy ΔG^0 is calculated using the thermodynamic equation [32]:

$$\Delta G^0 = -RT\ln K_e \qquad (4)$$

The value of the equilibrium constant K_e (L/mg) is given by the relationship:

$$K_e = \frac{q_e}{c_e} \qquad (5)$$

ΔG^0 is a parameter that enables to appraise the spontaneity of a chemical reaction. This variation in energy is determined from the following relationship:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (6)$$

Equation (5) can be written:

$$\ln K_e = -\frac{\Delta G^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (7)$$

R is the constant of perfect gas (R = 8.314 J/mol.K.) and T, the absolute temperature (K)

In this study, the phenol adsorption capacities on activated carbons CS_1 and CS_2 in solutions of initial concentration 20 and 10 mg.L^{-1}, are evaluated at temperatures of 27°C, 35°C, 40°C and 50°C

3. Results and Discussion

3.1. Iodine Value and Yield of Activated Carbons

Figure 1 shows the variation of the iodine value of the activated carbon obtained for different ratios of impregnation Xp. The maximum of iodine value 893 mg.g^{-1} is obtained in the series of SR_{2N} with Xp = 2.5. For this series, the iodine value increases from 827 mg.g^{-1} to 893 mg.g^{-1} when Xp increases from 1.5 to 2.5; then decreases from 893 mg.g^{-1} to 700 mg.g^{-1} when Xp increases from 2.5 to 4. The lowest values of iodine are obtained with activated carbons SR_{0N}. For this series of AC, iodine value increases from 280 to 380 mg.g-1 when Xp increases from 1.5 to 2.5; then drops to 267 mg.g^{-1} with Xp = 3 before taking the maximum iodine value of 569 mg.g^{-1} with Xp = 4. Also in the series of SR_{1N} maximum iodine value 866 mg.g^{-1} is obtained with Xp = 4. Indeed, the maximum iodine value is obtained for a ratio of impregnation Xp = 4, in a study conducted by Wang et al. [33] on rice bran with N 1soda solution pretreatment followed by phosphoric acid activation. Furthermore, based on figure 1, we note that the maximum of iodine value of the SR_{0N} series is less than the minimum values of SR_{1N} and SR_{2N} series. It can be concluded that pretreatment with soda has helped foster a better adsorption of iodine and therefore the development of the microporosity. Furthermore we notice that when the concentration of the soda solution goes from 1 M to 2 M, iodine value of CS_1 and CS_2 are almost identical if

impregnation Xp ratios go from 4 to 2.5. It therefore appears that the increase in the concentration of the soda solution during pretreatment enables a better development of the microporosity by decreasing the ratio of impregnation. Indeed, it was established that iodine value measures porosity for pore size ≥ 1.0 nm [14, 34]. Furthermore, according to Wang et al., (2010) [33], on the preparation of activated carbon by chemical way with H_3PO_4 from hydrochars rice bran (impregnation ratio 2.5: 1, carbonization at 500°C for 1 h) obtained carbon is very microporous with specific surface area $S_{BET} = 2700$ m^2.g^{-1} [33]. There is a proven correlation between the iodine value and specific surface area [34, 35].
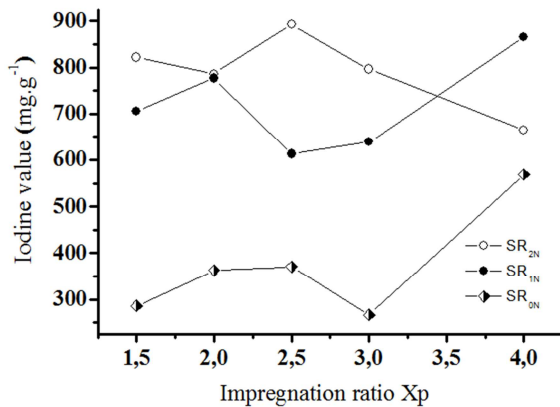

Figure 1. *Effect of impregnation ratio Xp on iodine value of activated carbons from the SR$_{0N}$, SR$_{1N}$ and SR$_{2N}$ series.*

Figure 2 shows the variation of the mass performance based on ratios of impregnation for three series of activated carbons SR$_{0N}$, SR$_{1N}$ and SR$_{2N}$. Indeed, the mass performance is an important measure of the feasibility in the preparation of activated carbon from a given precursor. According to Guo and Rockstraw, (2007) [30], large differences in mass performance can be observed on the basis of the precursor and preparation conditions (proportion of the impregnating agent, temperature of carbonization and activation, etc.). It appears from figure 2 that rice bran that has not gone through pretreatment with NaOH soda gives the greatest mass performance values (37.3 to 56.6%). In contrast rice bran that went through pretreatment with soda the mass performance barely exceeds 18%. For the same ratio Xp, the difference between the mass performance of series SR$_{1N}$ and SR$_{2N}$ is not significant; which indicates that the concentration of the NaOH solution has a lesser influence on the mass performance. Similarly, for a same concentration of soda solution, the effect of the Xp impregnation ratio on mass performance is not very significant. Indeed, the low mass performance of SR$_{1N}$ and SR$_{2N}$ series is linked to the elimination of SiO$_2$ silica in ash which represents a significant component of rice bran. According to studies conducted by Daifullah et al., (2003) [36], SiO$_2$ silica represents 94.5 of the 10.54% in mass of ash from rice bran. During pretreatment, silica reacts with NaOH soda to form sodium silicate Na$_2$SiO$_3$ [18]. Na$_2$SiO$_3$ Sodium silicate is soluble in water, and can be eliminated by washing with water. The overall reaction of Na$_2$SiO$_3$ formation is given by:
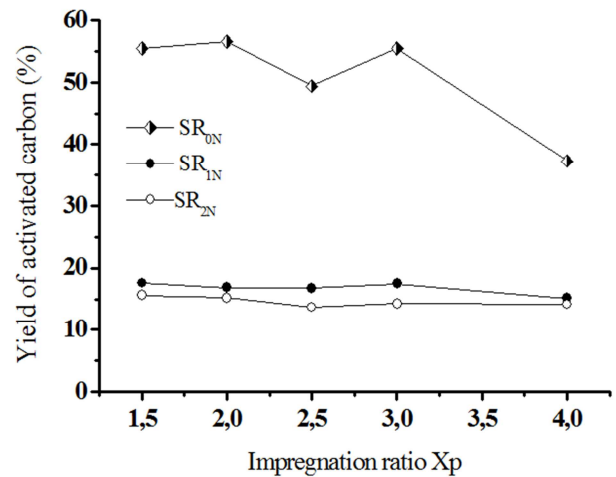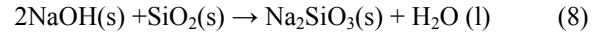
$$2NaOH(s) + SiO_2(s) \rightarrow Na_2SiO_3(s) + H_2O\ (l) \qquad (8)$$

Figure 2. *Effect of impregnation ratio Xp on yield of activated carbon SR$_{0N}$, SR$_{1N}$ and SR$_{2N}$ series.*

3.2. Textural Properties: Specific Surface Area and Porous Structure

Figures 3, 4 and 5 show nitrogen N$_2$ adsorption isotherms of the activated carbons in SR$_{2N}$, SR$_{1N}$ series and one of AC from the SR$_{0N}$ series respectively. Looking at the figures 3 to 5, we note that different activated carbon adsorption isotherms are type II according to the classification of Brunauer, Deming, Deming, and Teller (classification BDDT) [16]. Indeed, these isotherms are associated with adsorbents that possess a wide range of pore sizes such that adsorption may extend from monolayer to multilayer. Adsorption occurs first in monolayer and multilayer up to capillary condensation. These types of isotherms highlight formation of multi layers at low concentrations. This type of behavior reflects the existence of strong intermolecular interactions compared to the interaction between molecules and the solid. These isotherms show a nearly horizontal plateau for P/P$_0$ ranging from 0.3 to 0.7. There is then an increase of the slope at a relatively high pressure (P/P$_0$ > 0.8), which can be attributed to capillary condensation in the mesopores [37, 38].
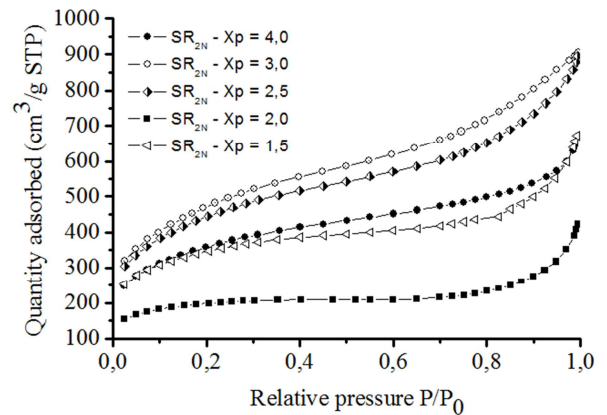

Figure 3. *Nitrogen N$_2$ adsorption isotherms of the activated carbons of SR$_{2N}$ series.*
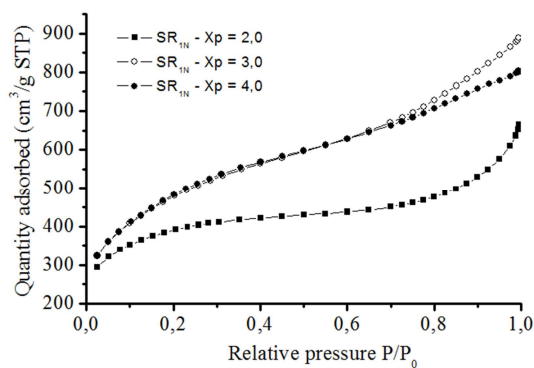
Figure 4. Nitrogen N_2 adsorption isotherms of the activated carbons of SR_{1N} series.
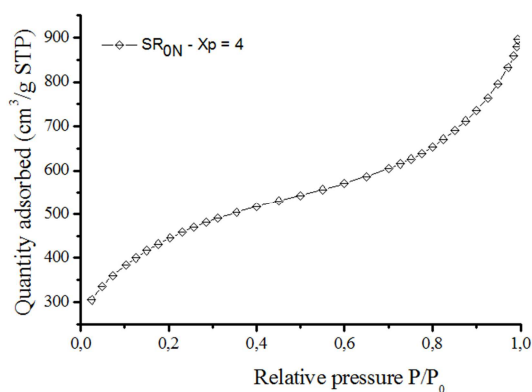

Figure 5. Nitrogen N_2 adsorption isotherms of the activated carbons SR_{0N} - Xp = 4.

On the other hand, figure 6 presents the nitrogen N_2 adsorption isotherms of the activated carbons CS_1 and CS_2. It is clear from this figure that activated carbon CS_1 has a slightly higher nitrogen adsorption capacity than that of carbon CS_2 for related pressures lower than 0.93. For relative pressures close to 1, CS_2 activated carbon becomes a little more adsorbent of N_2.
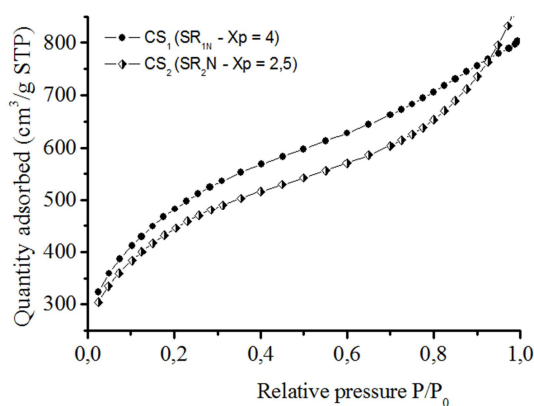

Figure 6. Nitrogen N_2 adsorption isotherms of the activated carbons CS_1 and CS_2.

Figure 7 shows the distribution of the size of the pores in the activated carbons CS_1 and CS_2 according to Horvath-Kawazoe method. The peaks of the volume of the pores around 11 Å are 0.045 $cm^3/g.Å$ for CS_1 and 0.027 $cm^3/g.Å$

for CS_2. In contrast the t-plot method indicates a CS_2 micropores volume greater than that of CS_1.

Table 1 shows the textural properties and those of the iodine value of activated carbons of SR_{2N}, SR_{1N} and SR_{0N} series. Activated carbons of the SR_{1N} and SR_{2N} series have developed a mesoporous texture with average diameters of pores ranging from 2.9 to 3.94 nm. In the SR_{1N} series we note that the BET surface increases as the Xp impregnation ratio increases from 2 to 4. However the volume of the micropores decreases with the increase in the Xp impregnation ratio. The Xp impregnation ratio = 4 corresponding to activated carbon CS_1 has the lowest pore diameter (Dp = 2.9 nm) and the largest specific surface area S_{BET} = 1771.6 m^2/g. For the SR_{2N} series, the lowest average pore diameter is also Dp = 2.9 nm. The specific surface area of activated carbon CS_2 (Xp = 2.5) is S_{BET} = 1558.5 m^2/g. The two activated carbons CS_1 and CS_2 have surface areas S_{BET} of the same order of size as those obtained by several groups of researchers such as Basta et al., (2009) [26] and Cyrus et al., (2006) [39]. However other groups of researchers found the values of specific surfaces areas of activated carbons relatively lower than those of the two activated carbons. These are Basta et al., (2009) [26] and Mohammad et al., (2007) [40]. The structural characteristics show that the two activated carbons CS_1 and CS_2 appear potentially more interesting for their very large BET surfaces and porous volumes and should have a greater capacity to adsorb a large number of molecules in their pores. However the activated carbon CS_1 seems more effective because it has more interesting structural features than those of the activated carbon CS_2.
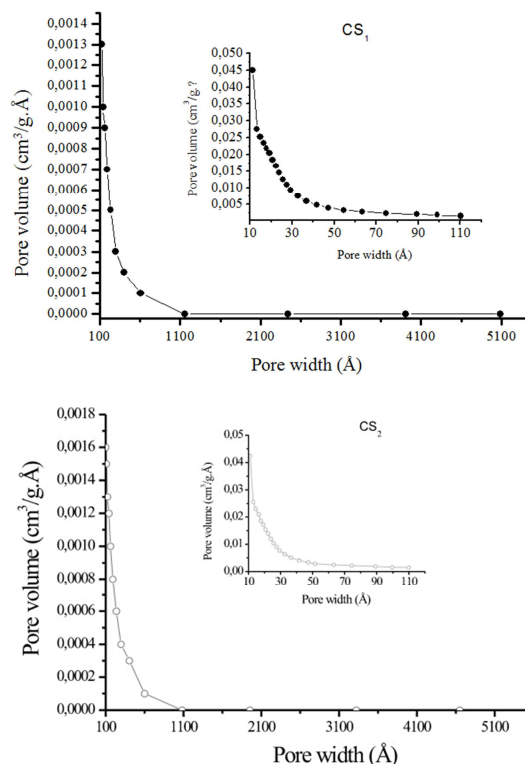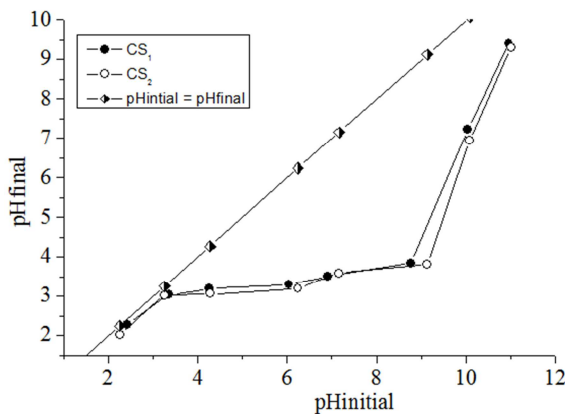

Figure 7. Distribution of the diameter of the pores of activated carbons CS_1 and CS_2.

Table 1. *Textural properties and iodine value of some activated carbons.*

| AC | Xp | I_2 (mg/g) | BET | | BJH | t-Plot | $V_{méso}/V_T$ (%) |
			S_{BET} (m^2·g^{-1})	V_T (cm^3·g^{-1})	Dp (nm)	$V_{méso}$ (cm^3·g^{-1})	V_μ (cm^3·g^{-1})	
SR_{2N}	1,5	822	1181.4	1.040	3.522	0.712	0.201	68.43
SR_{2N}	2,0	786	661.3	0.652	3.948	0.422	0.178	64.62
SR_{2N}	2,5	893	1558.5	1.385	3.554	1.057	0.143	76.345
SR_{2N}	3,0	796	1677.5	1.400	3.339	1.073	0.107	76.7
SR_{2N}	4,0	664	1251.3	0.993	3.176	0.715	0.138	71.97
SR_{1N}	2,0	777	1314.7	1.028	3.129	0.593	0.288	57.65
SR_{1N}	3,0	639	1688.4	1.374	3.256	1.050	0.114	76.42
SR_{1N}	4,0	866	1771.6	1.244	2.906	0.911	0.098	73.25
SR_{0N}	4,0	569	917.7	0.665	2.902	0.401	0.165	60.2

3.3. pH at Point of Zero Charge pH_{ZPC}

The representation of the final pH on the basis of the initial pH enabled us to determine the pH of zero charge. We fixed from Figure 8, the pH of zero charge which are 2.4 and 2.25 for activated carbons CS_1 and CS_2 respectively. These low values of pH_{ZPC} (2.4 and 2.25) of activated carbons CS_1 and CS_2 indicate their acid character [41, 42]. This result is consistent with that of the determination of the functional groups of surface by the Boehm method, which shows the dominance of acidic groups. Lower values of pH_{ZPC} (1.9 to 2.0), for carbons prepared by chemical activation with phosphoric acid from bark of jackfruit, have been reported by Prahas et al. [43]. In fact, the pH at point of zero charge is a very important parameter which indicates the acid-base behavior of finely divided solids. In studies of sorption it is a useful parameter that enables to assume on the ionization of functional groups on the surface area of activated carbons and on their interactions with the adsorbates. At pH_{ZPC}, charge of positive surface sites is equal to that of the negative surface sites [8].

Figure 8. *Curves for determination of pH_{ZPC} of activated carbons CS_1 and CS_2.*

3.4. Surface Chemical Functions by the Boehm Method

The determination of the surface functions enabled us to determine the nature and the quantities of the functional groups of activated carbon CS_1 and CS_2. Results are reported in table

2. The results of surface chemical analyses reveal that activated carbon CS_2 contains more acid functions (carboxyl, lactone and phenol) than activated carbon CS_1. There is a significant presence of carboxylic functions (more than 50% of surface acidic functions) for the two activated carbons.

Table 2. *Some chemical parameters of activated carbons CS_1 and CS_2.*

| Activated carbon | Iodine value (mg/g) | Surface functional groups | | | pH_{ZPC} |
		Carboxylic acid (meq H$^+$g)	Lactones (meq H$^+$g)	Phenolic (meq H$^+$g)	
CS_1	893	2.25	0.75	0.25	2.4
CS_2	866	4.25	2.0	0.50	2.25

3.5. Phenol Adsorption

3.5.1. Adsorption Isotherms

An activated carbon adsorption capacity is evaluated through its adsorption isotherm (Q_e according to C_e) which enables to describe the interaction between adsorbate and adsorbent and to optimize the use of the adsorbent. Langmuir and Freundlich isotherms models are used to describe the nature of the adsorption equilibriums. The Langmuir model is most frequently used for the adsorption of pollutants in solution. The Langmuir isotherm can be modeled by the equation (9):

$$Q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \tag{9}$$

With Q_e the quantity adsorbed at equilibrium per mass unit of the adsorbent in (mg/g), Q_0 adsorption capacity at saturation (mg/g), Ce the adsorbate concentration at equilibrium and K_L (L/mg) the adsorption equilibrium constant. The linear form of the Langmuir model is written:

$$\frac{C_e}{Q_e} = \frac{(1 + K_L C_e) \cdot C_e}{Q_0 K_L C_e} = \frac{1}{Q_0 K_L} + \frac{C_e}{Q_0} \tag{10}$$

In the case of an adsorbent with a heterogeneous adsorption surface (energetically different adsorption sites), the Freundlich adsorption model (equation 11) that is based on no particular theory is used:

$$Q_e = K_F C_e^{1/n} \tag{11}$$

With K_F (mg/g) the adsorption capacity, Ce (mg/L) concentration of adsorbate at the equilibrium and 1/n a constant indicating the adsorption intensity, the linearization of the Freundlich equation (equation 12) enables to determine the parameters K_F and 1/n.

$$\ln Q_e = \ln K_F + \frac{1}{n}\ln C_e \qquad (12)$$

The experimental results show that the phenol adsorption isotherm on the two activated carbons CS_1 and CS_2 is of type L, according to the Giles' classification [44]. It indicates a growth of adsorption when the adsorbate concentration increases (figure 9). These results (table 3) show that the adsorption of phenol on CS_1 and CS_2 is more in line with the Langmuir isotherm (R^2 > 0.99) [45] than the Freundlich isotherm (R^2 < 0.94) [46]. Adsorption intensity values (n) found (2.32 for CS_1) and 4 for CS_2 meet the condition of heterogeneity that is $1 < n < 10$ or $0 < n < 1$ [47]. The maximum adsorption capacity of activated carbon CS_1 (8,157 mg/g) is greater than that of activated carbon CS_2 (6.16 mg/g). This is in agreement with surfaces S_{BET} of the two activated carbons. However, the two values of maximum adsorption capacity are lower than those obtained by Lu and Sorial, (2004) [48], 13 mg/g for the phenol adsorption on activated carbon.

On the other hand, the value of K_F obtained for CS_2 (3.5) is greater than that of CS_1 (2.4). That indicates a greater affinity of phenol for CS_2 than for CS_1. Indeed, a group of researchers [49] reported that the structure of the pores of the adsorbent and the chemistry of the surface of the adsorbent determine the adsorption capacity of an adsorbate on an adsorbent. Particularly for phenol, it was reported by Salame and Bandosz, (2003) [50] that its adsorption is limited by the volume of micropores of activated carbons. Also, they said that because of their presence on the surface of activated carbon, carboxylic groups play two roles: (a) reaction of the carboxylic groups with phenol to form an ester bond; (b) removal by these carboxylic groups of electrons π from the matrix of aromatic activated carbon, causing a reduction in the strength of the interactions between the benzene ring of phenol and the "s" basic plans carbon, which reduces the phenol absorption, especially for the low concentration [51].
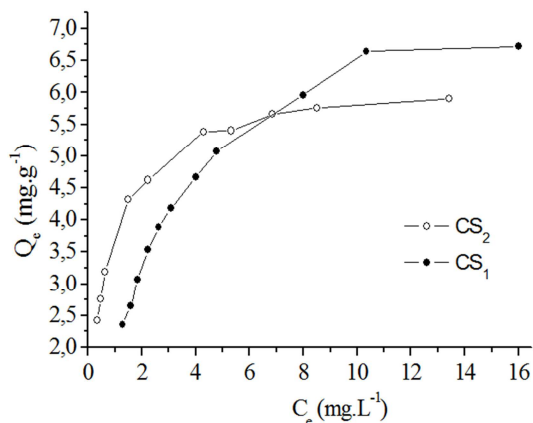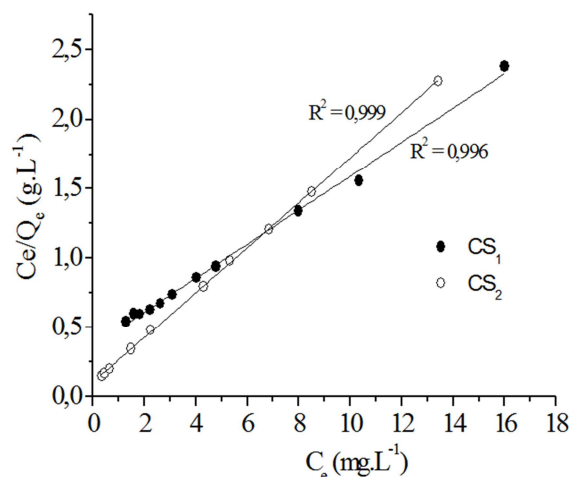

Figure 10. Linear form of the Langmuir model of phenol adsorption on activated carbons CS_1 and CS_2 with $C_0 = 20$ mg. L^{-1}.
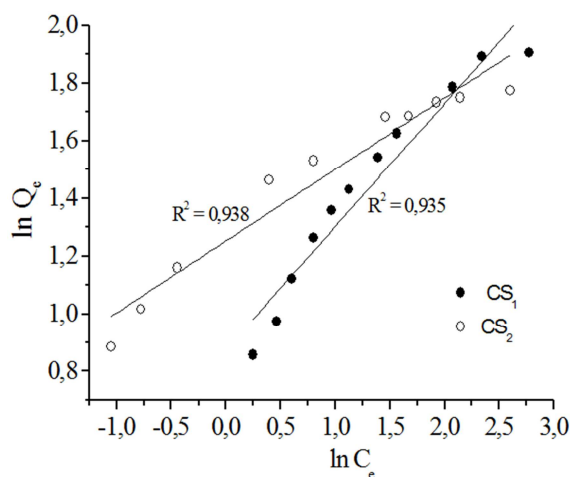

Figure 11. Linear form of the Freundlich model of phenol adsorption on activated carbons CS_1 and CS_2 with $C_0 = 20$ mg. L^{-1}.

Table 3. Values of the phenol adsorption parameters of Langmuir (q_m, K_L) and Freundlich (n, K_F) on activated carbons CS_1 and CS_2.

AC	Freundlich			Langmuir		
	k_F (mg$^{1-(1/n)}$.L$^{1/n}$.g^{-1})	1/n	R^2	q_m (mg.g^{-1})	K_L (g.L^{-1})	R^2
CS_1	2,4	0.43	0.935	8.157	0.335	0.996
CS_2	3,5	0.25	0.938	6.16	1.608	0.999

3.5.2. Thermodynamic Study of Phenol Adsorption

Figures 12 and 13 show the evolution of the equilibrium constant according to 1/T. ΔH^0 and ΔS^0 thermodynamic parameters have been determined from the slope and the ordinate at the origin of the $\ln_e = f(1/T)$ K curve. However the value of the variation in free energy of Gibbs ΔG^0 was calculated using equation (4). The values of the thermodynamic parameters of phenol adsorption on activated carbons CS_1 and CS_2 are grouped in table 4. ΔG^0 negative similar results have been reported by Mahapatra et al., (2012) [47] for the phenol adsorption on activated carbons. The negative value of the variation in free energy of Gibbs ΔG^0, indicates that phenol adsorption on these carbons is

Figure 9. Phenol adsorption isotherms by the activated carbons CS_1 and CS_2 ($C_0 = 20$ mg.L^{-1}, pH free).

spontaneous and thermodynamically favorable. This variation of free energy increases with temperature for the two activated carbons CS_1 and CS_2. That indicates that an increase in temperature is unfavorable for the process of phenol adsorption on the two activated carbons. Furthermore, the results in table 4 show that the variation in the Gibbs free energy ΔG^0 increases with the concentration of phenol, its adsorption at high concentrations will cause a large consumption of activated carbons.
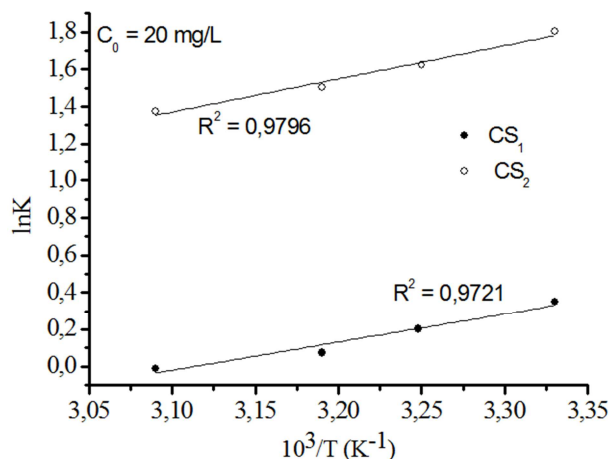
Negative values of the variation of enthalpy ΔH^0 indicate the exothermic nature of the adsorption and possibility of chemical adsorption in the range of temperatures selected for the study [32]. This confirms and justifies the reduction of the value of the adsorption capacity with temperature increase. Similar results have been reported by Ahmaruzzaman and Sharma, (2005) [52].
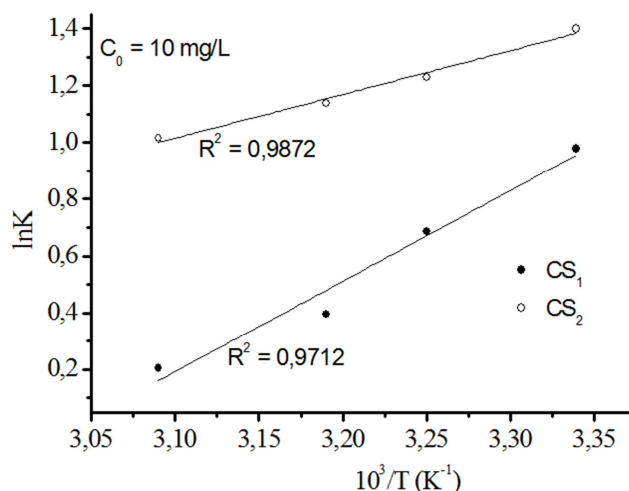

Figure 12. *Thermodynamic study of phenol adsorption on the AC $CS_1$and CS_2 (C_0 = 20 mg/L and a mass of 0 AC of 0.2 g / 100 mL).*

Figure 13. *Thermodynamic study of phenol adsorption on activated carbons CS_1 and CS_2 (C_0 = 10 mg/L and at a dose of 0.2 g/100 mL).*

Table 4. *Thermodynamic parameters for phenol adsorption on activated carbon CS_1 and CS_2.*

C_0 (mg.L^{-1})	T (K)	ΔG^0 (kJ/mol)		ΔH^0 (kJ/mol)		ΔS^0 (J/mol.K)		R^2	
		CS_1	CS_2	CS_1	CS_2	CS_1	CS_2	CS_1	CS_2
10	300	- 3.01	- 3.35	- 23.72	- 24.33	- 69.00	- 69.92	0.970	0.984
	308	- 2.46	- 2.79						
	313	- 2.12	- 2.45						
	323	- 1.43	- 1.75						
20	300	- 0.84	- 4.45	- 13.16	- 14,79	- 41.04	- 34.46	0.972	0.980
	308	- 0.52	- 4.18						
	313	- 0.31	- 4.00						
	323	- 0.10	- 3.66						

Negative values of ΔS^0 show a high probability of the presence of phenol molecules at the solid/solution interface during the adsorption process [53]. The negative value of ΔS^0 reflects the random decrease at the solid / solution interface of phenol with some structural changes in the adsorbate and adsorbent in the adsorption process. The same phenomenon has also been observed in the adsorption of orange acid 52 dyes by powder from leaves of Paulownia tomentosa Steud [54].

4. Conclusion

The findings of this work show that activated carbons from the rice bran passing through pre-treatment with soda have the best structural characteristics. Caustic pretreatment has developed a better porosity of activated carbons. Indeed the maximum iodine value fell from 569 mg.g^{-1} with the series not having soda (SR_{0N}) pre-treatment to 866 and for

893 mg.g^{-1} for series SR_{1N} and SR_{2N} with a prior leaching soda 1N and 2N respectively. Similarly the specific surface S_{BET} has improved from 917 to 1711.6 $m^2.g^{-1}$ with this operation. Any time beyond a given dose, the soda is unfavorable to the improvement of the specific surface area of activated carbon products. For the same ratios of impregnation with phosphoric acid, specific surfaces of the carbons of the SR_{2N} series are relatively smaller than those of the SR_{1N} series. It also appears that the soda solution enables not only to eliminate the ashes but also facilitates a reorganization of the structures of the polysaccharides with the decrease in the ratio of impregnation as an advantage. However, pretreatment reduces the mass performance of activated carbon.

On the other hand, the activated carbons CS_1 (SR_{1N} - Xp = 4) et CS_2 (SR_{2N} - Xp = 2,5) have specific surface area equal to 1711.6 and 1558.5 m $s^2.g^{-1}$ and the porous volumes are 1.234 and 1.385 cm^3/g respectively. The study of the

adsorption isotherms confirms that activated carbon CS_1 is slightly more effective than activated carbon CS_2 because it has a big BET surface and a much larger pore volume. Furthermore, the adsorption of phenol by two carbons is well described by the kinetic models of Langmuir and Freundlich. Thermodynamic study reveals that the adsorption of phenol on the two activated carbons is spontaneous and exothermic.

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