Scientific
Research
Publishing

Preparation and Characterization of Activated Carbon Based on Wood (*Acacia auriculeaformis*, Côte d'Ivoire)

Drissa Ouattara Kra[1], N'guadi Blaise Allou[1], Patrick Atheba[1,2*], Patrick Drogui[2], Albert Trokourey[1]

[1]Laboratoire de Chimie Physique, Université Félix Houphouët Boigny de Cocody-Abidjan, Abidjan, Côte d'Ivoire
[2]Institut National de la Recherche Scientifique (INRS-ETE), Université du Québec, Quebec City, Canada
Email: *grahpatrick.atheba@gmail.com

Abstract

The objective of this work is to prepare one of the best activated carbon (CA) based on wood (*Acacia auriculeaformis*). The chemical activation method was used for varying the chemical agent namely phosphoric acid H_3PO_4 (CAA), sodium hydroxide NaOH (CAB), and sodium chloride NaCl (CAS). The physico-chemical analysis of the three activated carbons indicated that, under the conditions of preparation, the activated carbons possess activation efficiencies lower than 50% (41.81% for CAA, 26.25% for CAB and 48.87% for CAS), low ash content (CAA: 5.00%, CAB: 14.90 and CAS: 6.60%) and iodine values ranging from 190.35 mg/g to 380.71 mg/g, suggesting that the good quality of the prepared activated carbon. The surface functional groups using Boehm test and the zero point charge (pH_{ZPC}) methods confirmed the acidic, basic and neutral character for CAA, CAB and CAS respectively (CAA: $pH_{ZPC} = 4.8$, CAB: $pH_{ZPC} = 8.2$, CAS: $pH_{ZPC} = 6.8$). The surface specific areas were determined through the liquid phase adsorption of acetic acid and methylene blue using the Langmuir method and BET analysis. Also, the porosity was determined. The BET surface areas of CAA, CAB and CAS were respectively 561.60 m^2/g, 265.00 m^2/g and 395.40 m^2/g. The influence of chemical activation agent on pores formation was confirmed by scanning electron microscopic (SEM) analysis. CAA was selected as the best activated carbon because of its good surface area and good pore volume compared to those found in the literature. Therefore, its application as an adsorbent for effluents treatment could be explored. In addition, the best activating agent for coal from *Acacia auriculeaformis* was found to be phosphoric acid.

1. Introduction

The increase of industrial sites and human activities has negatively impacted the environment, due to the large quantities of toxic species generated and released in the wild in different forms (solid, liquid and gaseous). This constitutes a great concern for public authorities, by the consequences which may occur on living species and their environment.

Currently, industrial wastewater discharges containing relatively large quantities of toxic substances is a growing concern. Their presence in effluents is a threat to any biological organism. Water becomes a vector of pollution. To avoid the toxic effects of these substances and to protect the environment, it is necessary to treat contaminated effluents before their release in the natural environment. Scientists from diverse backgrounds are interested in the identification and removing pollutants directly involved in ecosystem unbalances. Physical or chemical processes have been widely used to remove pollutants from wastewater. These methods include: coagulation-flocculation [1], biological treatments (biodegradable pollutants) [2], electrochemical methods [3] [4], membrane processes [5], adsorption [6] [7]. The use of activated carbon in the adsorption process is in great demand.

In the last decades, activated carbon has attracted a lot of attention because of its versatile application in materials science, meeting various criteria required for new materials [8]. Indeed, activated carbon is a highly porous carbonaceous, hydrophobic, and non-polar adsorbent prepared to obtain a high degree of porosity which confers to it a considerable surface area. Activated carbon is one of the most commonly used adsorbents in many liquid and gas phase applications for its adsorbent properties related to porosity and surface area. The diversity of its applications, its impact on industrial development and health show its importance in our days. It is widely used in environmental technology because of its ease use in the removal of organic and inorganic compounds from aqueous effluents [9]. Activated carbon is one of the most effective material used to remove a wide range of contaminants. It can be used to treat some or all the contaminants, either directly or in combination with other processes. Its utility is no longer to prove. However, because of the high cost of preparation of activated carbon which restricts its frequent use, several scientists have studied this problem in order to find low-cost precursors to prepare activated carbon. Thus, several studies have been conducted in this direction to prepare activated carbons from plant materials such as rice straw [10], coconut shell [11] [12] [13], tamarind wood [14] [15] and from mineral materials [16]. Their production can be

done in two ways, either by physical activation or chemical activation. The physical activation results from the heat treatment and consists of two basic processes: carbonization or pyrolysis and activation. As for the chemical activation, different chemicals such as KOH [17], NaOH [18], $ZnCl_2$ [19], H_3PO_4 [20] have been used as activation agents. In addition, the efficiency of activated carbons prepared by chemical activation is about 3.7 times greater than those obtained by physical activation [21].

As a part of the search of natural resources for the local production of cheaper activated carbon, *Acacia auriculeaformis* wood has attracted our attention because of its abundance. Furthermore, its use is very often limited to carpentry and fuel (firewood or charcoal for cooking). Our previous work [22] deal with the adsorbent properties of the active carbons of *Acacia auriculeaformis* and *Acacia mangium* by methylene blue adsorption. However, using *Acacia auriculeaformis* as a source of activated carbon production in future applications could be a problem due to deforestation. Therefore, to overcome this eventuality, this species of *Acacia* could be recommended to farmers as a plantation tree because of its rapid growth even on poor soils. Thus, although this material serves as a precursor of activated carbon, it could also be a source of income for farmers.

The present work focused on the preparation and characteristics comparison of *Acacia auriculeaformis* activated carbon resulting from chemical activation with three different activation agents. H_3PO_4, NaOH and NaCl were chosen as activation agents. The objective of this work is to valorize *Acacia auriculeaformis* charcoal in activated carbon with a view contributing to domestic and industrial waste water treatment.

2. Materials and Methods

2.1. Materials and Carbonization

The precursor of the activated carbons is a charcoal made from the carbonization of Acacia wood (*auriculeaformis* of 8 to 9 years old) taken from Anguédedou forest located at three kilometers to Abidjan (Côte d'Ivoire). This charcoal was prepared in an experimental butane gas retort at CNRA (National Center for Agronomic Research) Technology Research Station (SRT), Cocody, Abidjan. Acetic acid (99.5%, from Carlo Erba), methylene blue (from Merck Eurolab), phosphoric acid (85%, from Panreac, Spain), sodium hydroxide (95%, from Scharlau, Spain) and sodium chloride (99.6%, from Alpha Chemika, India) all A.R. grade, were purchased from Poly Chimie, Abidjan, Cote d'Ivoire. Distilled water was used for solution preparation.

For carbonization, acacia woods were exposed to ambient air for sun drying for 3 months in order to obtain humidity level of 20% to 25% recommended for good mass yield during the carbonization process [23]. The sun-dried acacia woods were cut into almost parallelepiped shaped pieces with 10 cm long, 8 cm wide and 5 cm thick, then baked and charred in a furnace heated by an external furnace fed with butane gas. The temperature was read each 15 minutes using

the thermocouple in order to control the carbonization process and to determine the carbonization time. Thereby, the carbonization temperature reached a plateau of 350°C after 3.5 hours of carbonization. The carbon was removed after a period of 4 hours of the plateau.

2.2. Activation

Chemical activation was used according to the methods described by Kra *et al.* [22] and Kaledia *et al.* [24] using chemical agents such as H_3PO_4, NaOH and NaCl. The raw charcoal was ground. One of the first two steps of the methods described consists in impregnation of the raw precursor in an aqueous solution of the activating agent and the second one in the heat treatment of the impregnated carbons.

2.2.1. Impregnation

Activation in acidic medium was done following the protocol reported [22]. Thus, in 1 L beaker, 30 g of ground charcoal and 400 ml of 10% phosphoric acid solution were mixed. For NaOH activation, the method proposed by Kaledia *et al.* [24] was followed. Therefore, 30 g of crushed raw charcoal were dispersed in 400 ml of 1M solution of sodium hydroxide. As for NaCl salt activation, a saturated saline solution was prepared by dissolving approximatively 14.6 g of NaCl in 400 ml distilled water. Then, 30 g of ground raw material are impregnated in the prepared solution. In each case, after stirring for 30 min at 350 rpm, the mixture was kept standing for 24 hours. Finally, the slurry obtained was filtered and dried in an oven (MEMMERT) at 105°C for 24 hours. The dry residue was crushed and only the fraction of particles with the diameter between 125 μm and 2 mm were recovered using an AFNOR sieve.

2.2.2. Heat Treatment

The dry sample obtained after impregnation was placed in a muffle furnace (NABERTHERM mark 30°C - 3000°C) at 800°C for 6 hours for heat treatment. The choice of the duration and the temperature of the heat treatment were inspired by the work of Kra *et al.* [22]. The charcoal, once taken out of the oven at room temperature, was thoroughly washed with hot distilled water until the filtered water pH was between 6.5 and 7. The sample was then dried in oven at 105°C for 24 hours. Activated carbon is stored in hermetically sealed jars prior to testing after cooling in a desiccator. In this work, the modified carbons were called CAA (activation with H_3PO_4, acid), CAB (activation with NaOH, base) and CAS (activation with NaCl, salt). The same process was followed for each sample.

2.3. Characterization of Activated Carbons

2.3.1. Activation Efficiency

The activation efficiency R (%) is defined as the mass ratio of activated carbon produced after activation to the mass of the raw material used before activation.

The yield values of the activated carbons product are estimated by application of the following Formula (1):

$$R\left(\%\right) = \frac{\text{activated carbon mass}}{\text{precursor mass}} \times 100 \tag{1}$$

2.3.2. Ash Content

The ash content C (%) was determined according to ASTM (American Standards Technology Method) described as below. In a dry crucible of mass m_0, 1 g of carbon sample is placed and weighed as m_1. The crucible is then placed in the muffle furnace at 650°C for 7 hours until the ash is obtained. After cooling it is weighed as m_2. The ash content is calculated from the Formula (2):

$$C\left(\%\right) = \frac{m_2 - m_0}{m_1 - m_0} \times 100 \tag{2}$$

2.3.3. Determination of Iodine Number

Iodine value is the most fundamental parameter used to measure the performance of activated carbon in terms of activity. The higher the value of iodine value, the higher the degree of activated carbon activity. Iodine number (mg/g) is the amount of iodine (I_2) adsorbed (mg) per gram of charcoal in aqueous solution 0.02N iodine. It characterizes the zones accessible to any particle of size less or equal to that of the iodine molecule [25]. The iodine value was determined based the method which is an adaptation of the 1989 CEFIC method and the AWWA B600-76 standard applied by Mamane *et al.* [26] during the preparation and characterization of activated carbon based on hulls of Balanites Eagyptiaca and Zizyphus Mauritiana. Therefore, 0.2 g of activated carbon was placed in 100 ml beaker containing 20 ml 0.02N iodine solution and stirred for 4 to 5 minutes. Then, filtered and 10 ml of the filtrate were collected and tested with 0.1N sodium thiosulfate solution in the presence of two drops of starch paste until the solution completely discolored. From the reaction of I_2 on sodium thiosulfate whose equation-balance (3), the remaining concentration in I_2 (C_{I_2}) was calculated and the iodine number (Q_{I_2}) was determined from Formula (4).

$$2NaS_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI \tag{3}$$
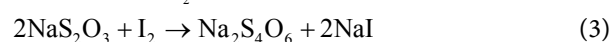
$$Q_{I_2} = \frac{\left[C_0 - \dfrac{C_n \cdot V_n}{2V_{I_2}}\right] * M_{I_2} * V_{abs}}{m} \tag{4}$$

where V_n (ml) is the volume of sodium thiosulfate poured at the equivalence, C_n is sodium thiosulfate concentration, C_0 is I_2 initial concentration, V_{I_2} is I_2 dosed Volume, M_{I_2} is iodine Molar mass (253.81 g/mol), V_{abs} is adsorption volume (20 ml) and m (g) is activated carbon mass.

2.3.4. Chemical Characterization

1) Surface Functional Groups

The measurements were done according to Boehm method [27] [28]. This method was used to determine the composition of activated carbons in acidic or

basic surface functional groups. To neutralize the acid groups, 0.1N solution of strong bases such as $NaHCO_3$, Na_2CO_3 and NaOH were prepared. As far as 0.1N solution of HCl was used to neutralize the basic groups. For each sample, 1 g was suspended in 50 ml of the prepared solution and maintained in constant agitation during 72 hours. After filtration, a back titration with NaOH (0.1N) or HCl (0.1N) solution, help to determine the number of sites of the acidic or basic functional groups through the Formula (5) below:

$$N_0V_0 - N_fV_0 = n_{geq}(R) \qquad (5)$$

in which, N_0V_0 represents the number of gram equivalent before the reaction, N_fV_0 is the number of gram equivalent after the reaction and $n_{geq}(R)$ is the number of gram equivalent reacted.

2) Determination of point zero-charge pH (pH$_{ZPC}$)

The pH$_{ZPC}$ or pH of zero point charge corresponds to the pH value for which the net charge at the activated carbon surface is zero. Then, 100mg of activated carbon and 50ml of 0.01M NaCl solution of pH ranging from 2 to 12, pH adjusted by addition of 0.01M HCl or NaOH solution [29], were kept in constant stirring at room temperature for 48 hours and the final pH was measured. The pH$_{ZPC}$ is the point where the pH$_{final}$ = f (initial pH) curve intercepts the first pH$_{final}$ bisector = f (initial pH).

2.3.5. Surface Characterization

1) Surface morphology of activated carbon

Scanning electron microscopy (SEM) was used to determine the morphology structure of the prepared samples. Images were collected using JSM-840 model.

2) Specific surface area

The determination of the specific surface area of activated carbons was carried out on the one hand, according to the Langmuir model based on the adsorption method of acetic acid (AC) and methylene blue (BM) [30] [31] and on the other hand by the method developed by Brunauer-Emmet-Teller, commonly called BET method [32]. Regarding the specific surface area related to AC and BM adsorption, it was necessary to determine the equilibrium time, then the adsorption isotherms according to Langmuir model and finally the maximum adsorption capacity Q_m. Knowing Q_m, the specific surface could be calculated with the following Formula (6):

$$S_L = Q_m \cdot \delta \cdot N \qquad (6)$$

with S_L the specific surface area (m²/g), Q_m the maximum adsorption capacity (mol/g) or (mg/g), δ area occupied by acetic acid or methylene blue (m²) (acetic acid area = 21 Å² and methylene blue area = 175 Å²) and N Avogadro Number (mol^{-1}).

For this purpose, 1 g of activated carbon was suspended into 50 ml of acetic acid or methylene blue (C_0) and stirred. At different interval times of 5, 10, 30, 45 and 60 min samples were collected and the residual concentration was calculated. The process of the isotherm was almost similar to that of the adsorption kinetic. 50 ml of acetic acid or methylene blue at various initial concentrations

with 1 g activated carbon under constant agitation during the equilibrium time calculated during the kinetic.To determine the residual concentration at equilibrium C_e, the filtrate was titrated volumetrically in presence of phenolphthalein for acetic acid and spectrophotometrically with a Helios OMEGA type spectrophotometer at a wavelength of 665 nm for methylene blue. The amount of adsorbed adsorbate was determined from Equation (7):

$$q_e = \frac{C_O - C_e}{m} \cdot V \tag{7}$$

BET surface area, pore volumes and pore dimensions were calculated from nitrogen adsorption isotherms at 77 K. The samples were analyzed using a Quantachrom Autosorb 1 device (Chemical Engineering Department, Laval University). The total pore volume is determined by the method of the adsorbed amount of nitrogen at $P/P_o = 0.99$. The microporous volume is determined by applying the Dubinin-Radushkevich model to the adsorption isotherm.

3. Results and Discussion

3.1. Physico-Chemical Analysis: Yield, Ash Content and Iodine Value

Table 1 shows activation efficiency, ash content and iodine value of carbons activated with three different chemical agents. From Table 1, it can be seen that the activation efficiencies of the prepared activated carbons are less than 50% indicating the formation of micropore and mesopore [33]. In the three cases of activation, the best yields are obtained with the acidic agent and salt activating agent. However, the mass yield related to the salt is greater than that of the acid. This could be explained by combustion reactions that are very pronounced with H_3PO_4 because of its low stability temperature (boiling temperature 213˚C against 1465˚C for NaCl). Similar observations were reported by Haimour and Emeisch [34]. The weak mass yield obtained with NaOH (26.25%), could be due to the fact that NaOH is a strong base, corrosive base and stable product that can melt at 318˚C. At temperatures above 360˚C, this molten hydroxide reacts easily with most of the raw materials containing carbon (carbon, lignocellulosic materials, ...) [35] and certainly accelerates the combustion. Since the yield is an indicator of the performance of the preparation method of the material especially on an industrial scale, one can note that NaOH activating agent does not have a major advantage in terms of activated carbon gain because of its low yield. The difference in yields observed suggests that the nature of the chemical activation agent used during the impregnation could be involved.

Table 1. Physico-chimical parameters of the prepared activated carbon.

Activated carbon	Activation efficiency (%)	Ash content (%)	Iodine number (mg/g)
CAA	41.81	5.00	304.57
CAB	26.25	14.90	190.35
CAS	48.87	06.60	380.71

Ash levels (5% for CAA, 6.6% for CAS and 14.9% for CAB) are relatively low. One of the parameters influencing the adsorption properties of coal is its ash content. This parameter has a significant effect on the quality of activated carbon. It appears that a high ash content decreases the specific surface area. Therefore, the ash content of a good adsorbent must not be too high, *i.e.* less than 20% [36]. An excessively high ash content (>20%) reduces coal activity, its potential reactivation and can generate leakage of impurities (mineral salts). The ash value reported in this study is an indication for good adsorption capacity of the synthesized activated carbons. In addition, this study shows that activation with phosphoric acid shows low ash content compared to the two other activating agents. This could be assigned to the corrosive action of phosphoric acid which eliminates impurities on precursors [37]. CAB ash rate slightly high compared to the two others suggests that this coal is still rich in the mineral matter after activation. The nature of the chemical agent, therefore, has a considerable influence on the ash content.

Activated carbons with different agents contain pores accessible to iodine molecules. The iodine number values was 304.47 mg/g, 190.35 mg/g and 380.71 mg/g respectively for CAA, CAB and CAS. Similar iodine number (319.67 and 286.26 mg/g) were reported during the characterization of acacia activated carbons prepared with basic agents [8]. The determination of porosity with iodine index helps to define, on the one hand, activated carbons containing many macropores and mesopores (low iodine index), and on the other hand, activated carbons containing mainly micropores (high iodine value). The order of iodine value CAB < CAA < CAS indicates that chemical activation leads to the creation of new pores as well as to the enlargement of available pores. From the three prepared activated carbons, those activated with H_3PO_4 and NaCl have greater I_2 adsorption capacity [26]. It has been found from the literature that activated carbon with iodine value higher than 950 mg/g are mainly used to measure micropores (0 - 20 Å) present in the inner surface of the coal [38]. The obtained values are below this value, suggesting that out of micropores created, the presence of mesopores and macropores is expected.

A comparative study of the three characteristics studied reveals that CAA and CAS show high I_2 adsorption capacity, low ash content and high yield contrary to CAB.

3.2. Chemical Analysis: Surface Functional Groups and Zero Point Charge pH

The amounts of functional groups of the prepared carbons are given in Table 2. The results of the chemical analysis revealed that CAA has an acidic functional group on the surface (total acid = 1.85 meq/g), particularly carboxylic and phenolic functions. This is due to the chemical activation with phosphoric acid. However, CAB possesses basic surface functional groups (total basic = 1.18 meq/g) attributed to the basic impregnating agent. The basicity of the sample is partly due to the free oxygen of the basic Lewis sites, which is often attributed to

Table 2. Surface functional groups and zero point charge pH of the prepared activated carbons.

| Carbon | Functional group (méq·g^{-1}) | | | | | pH$_{ZPC}$ |
| | Acid | | | | Base | |
	carboxylic	Lacton	Phenol	Total	Total	
CAA	0.75	0.40	0.70	1.85	0.18	4.8
CAB	0.00	0.35	0.00	0.35	1.18	8.4
CAS	0.00	0.00	0.80	0.80	0.69	6.8

the π electrons of the graphitic planes [39]. With regard to the acid functions for CAB, the lactone group is more. As for CAS, the surface functions are almost neutral (slightly acidic and among the acids, the phenolic groups dominate). Therefore, it can be concluded that it behaves like an acid, then as a base (amphoteric behavior). According to the literature [40], as adsorption is a surface phenomenon, carbons with acidic surface groups (CAA) will have cation exchange properties, whereas those with a basic character (CAB) will have anion exchange properties.

The pH$_{ZPC}$ value helps to determine the acidic or basic character of activated carbon and to know, according to the pH of the solution, its net surface charge. If both, carbon and pollutant molecule, are charged, electrostatic type interactions may exist and explain (in part) preferential or disadvantageous adsorption [41]. The above values (Table 2) were obtained using the curves in Figure 1. CAA has acidic pH$_{ZPC}$ while CAB is basic indicating high oxygen content in CAA compared to CAB. However, the pH$_{ZPC}$ of CAS is very close to neutral medium. This value confirms the amphoteric nature of the CAS. It should be noted that there are some consistencies between the pH$_{ZPC}$ values and the proportions in acidic and basic functional groups [42] [43].

3.3. Surface Characterization: Surface Area, Porosity and SEM Analysis

3.3.1. Surfaces Area Related to Acetic Acid and Methylene Blue Adsorption

The kinetic curves for acetic acid and methylene blue adsorption on the various carbons given in Figure 2 show that the residual concentration decreases with time. After 30 min for acetic acid and 45 min for methylene blue, the residual concentration does not seem to change at all. These two times were used as equilibrium time for the isotherm studies.

Figure 3 shows the adsorption isotherms of acetic acid and methylene blueon various activated carbons (CAA, CAB and CAS). IUPAC classifies isotherms into six categories. All the curves in Figure 3 are similar to Type I isotherm of this classification [44]. This type of isotherms is observed in the case of adsorption of microporous solids having pores whose diameter is less than 2 nm. It is also observed in the case of monolayer adsorption. These isotherms of adsorption can therefore be described by Langmuir model.
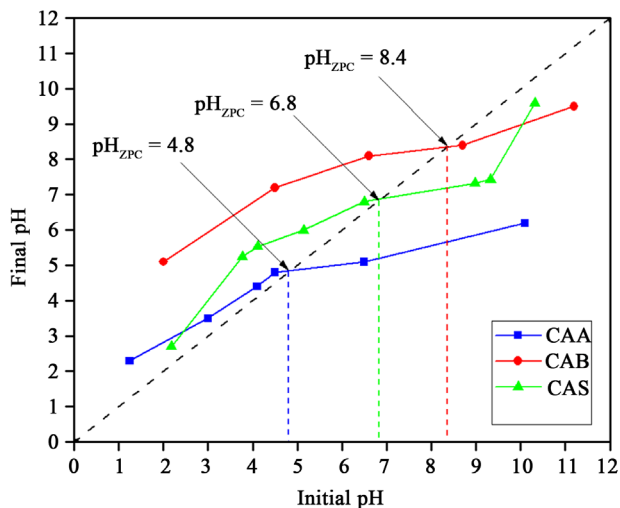
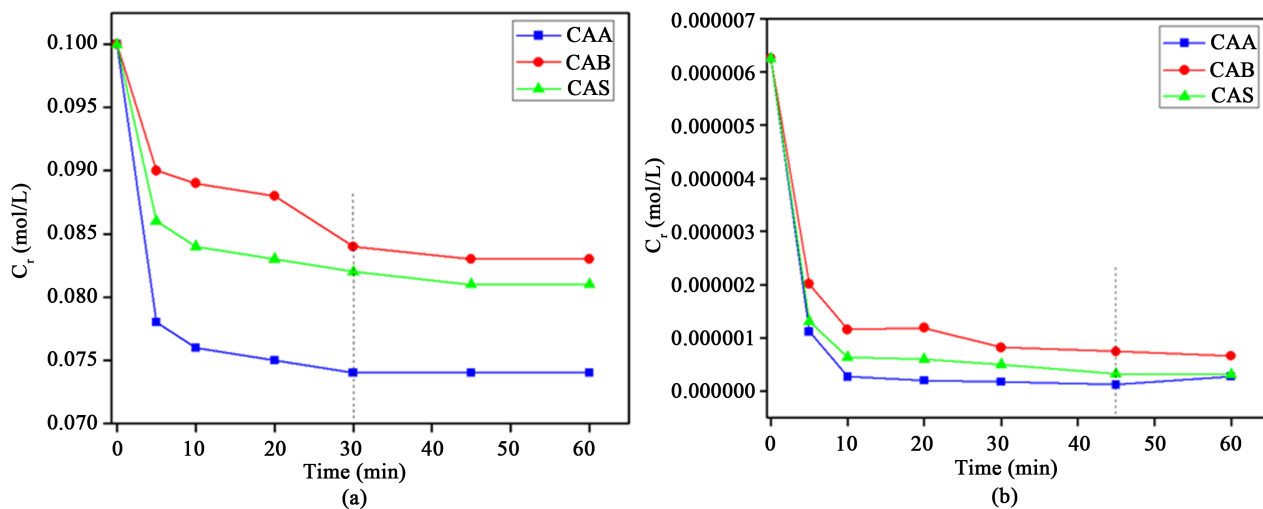**Figure 1.** Zero point charge pH for the different activated carbons.

Figure 2. Equilibrium time for (a) acetic acid adsorption and (b) methylene blue adsorption on different activated carbons.
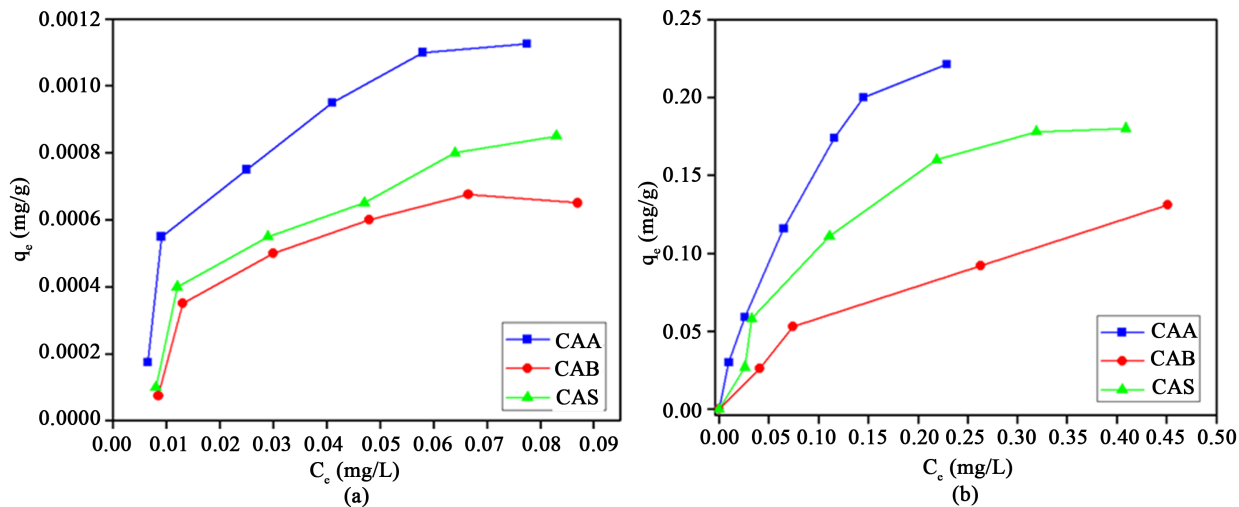

Figure 3. Adsorption isotherms for (a) acetic acid and (b) methylene blue on different activated carbons.

Figure 4 shows the linear representation of the adsorption isotherms according to Langmuir model. Table 3 indicates that the correlation coefficients (R^2) are close to 1. The adsorption of acetic acid and methylene blue on all the carbons can, therefore, be described by Langmuir model.

The maximum adsorption capacity Q_m of each carbon was determined to apply Langmuir isotherm model. High Q_m value implies good adsorption. The surface specific area offered by each carbon was calculated using Q_m and summarized in Table 3. The surface areas related to acetic acid and methylene blue adsorptions decrease in both case in the following order: CAA > CAS > CAB. It seems clear that CAA is the best one of the prepared activated carbon because of its high surface area related to acetic acid, suggesting significant microporous and some mesoporous adsorption. In addition, the large surface area related to methylene blue, indicating mesoporous adsorption. BET method is very accurate method for the determination of the surface area, therefore, it was used to verify the results obtained previously.

### 3.3.2. BET Specific Surface Area and Porosity

N_2 adsorption data were obtained from the Department of Chemical Engineering, Laval University, Quebec. However, N_2 adsorption isotherms at 77 K of the prepared activated carbons with different activating agents are shown in Figure 5 and pore properties are given in Table 4. These isotherms are type I according to IUPAC classification. The type I isotherm represents monomolecular

Table 3. Summary of the different surface areas obtained.

Carbon	Correlation coefficient (R^2)			Q_m (mmol/g)			S (m^2/g)		
	AC	BM	N_2	AC	BM	N_2	S_{AC}	S_{BM}	S_{BET}
CAA	0.991	0.992	0.994	4.407	0.0010	5.07	557.13	184.36	561.60
CAB	0.990	0.971	0.994	0.805	0.0005	2.42	101.77	92.18	265.00
CAS	0.956	0.994	0.995	0.950	0.0010	3.66	120.01	184.36	395.40
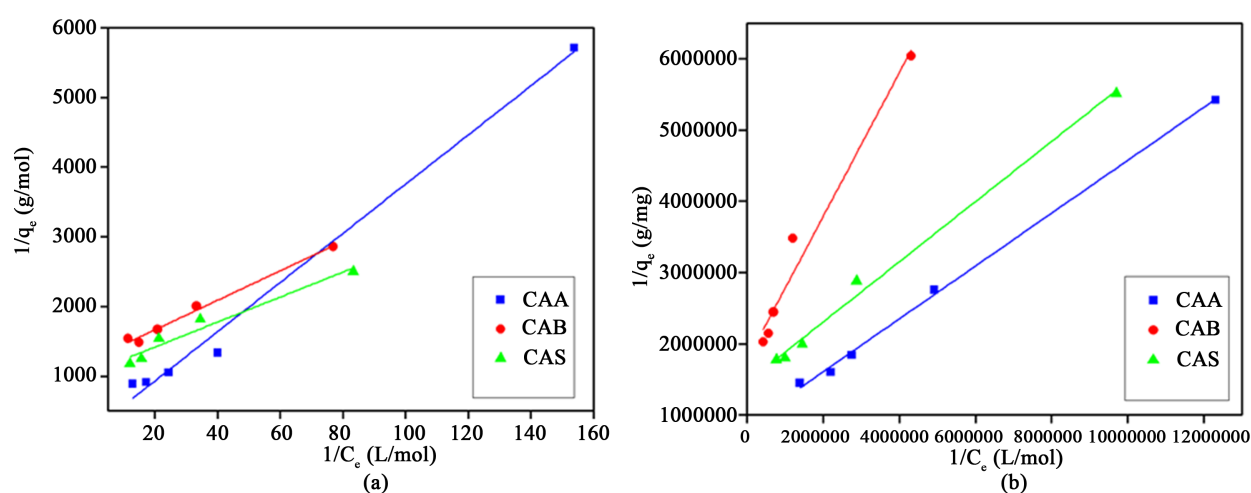
Figure 4. Langmuir isotherm model of (a) acetic acid and (b) methylene blue adsorptions.
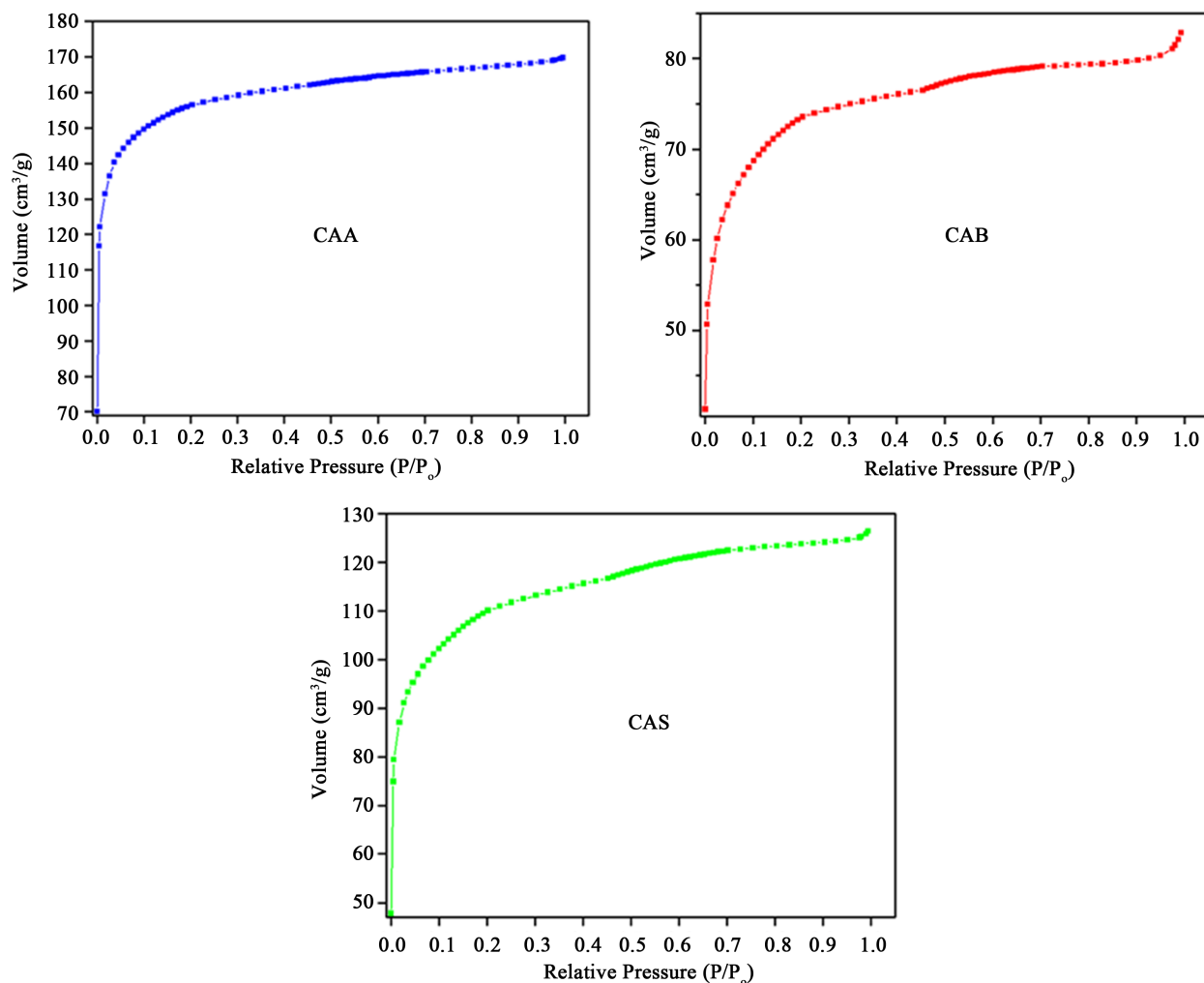
Figure 5. N$_2$ adsorption isotherm on CAA, CAB and CAS.

Table 4. BET and BJH surface properties of CAA, CAB and CAS.

Carbon	Pore volume (cm³/g)	Pore diameter (Å)	S_{BET} (m²/g)
CAA	0.26	11.26	561.60
CAB	0.13	11.78	265.00
CAS	0.20	11.77	395.40

adsorption and applies only to microporous adsorbents with small pore sizes. Therefore, it can be concluded that activated carbons prepared from the above methods are mainly microporous.

Specific surface areas are calculated according to BET method [32]. From the basic hypotheses of BET's theory, BET equation follows Equation (8):

$$\frac{P/P_o}{V \cdot (1 - P/P_o)} = \frac{1}{V_m \cdot C} + \frac{C-1}{V_m \cdot C} \cdot P/P_o \tag{8}$$

where V is the volume adsorbed at the pressure P, V_m is the volume of gas necessary to cover 1 g of adsorbent with a single layer of gas and C is BET con-

stant.

BET equation is valid for low relative pressures $P/P_o \le 0.35$. By plotting of $\dfrac{P/P_o}{V \cdot (1 - P/P_o)}$ versus P/P_o a straight line is obtained whose slope $\dfrac{C-1}{V_m \cdot C}$ and intercept $\dfrac{1}{V_m \cdot C}$ allow us to calculate V_m and C.

Figure 6 shows the linear representation of BET equation for the three prepared carbons. The linear fitting curves obtained seem to confirm our previous results (R^2 close to unit). The knowledge of V_m helps in the determination of Q_m and consequently BET surface area (S_{BET}) which is calculated using the following Equation (9):

$$S_{BET} = \sigma \cdot Q_m \cdot N \tag{9}$$

with σ area occupied by a molecule of N_2 vapor, N Avogadro Number (6.025×10^{23} mol^{-1}) and at $T = 77$ K, the surface of a nitrogen molecule is $\sigma = 16.2$ Å^2.

Table 4 indicates that CAA sample has a specific surface area higher than that of CAS and CAB samples and the same order is followed for N_2 amount adsorbed. This would be assigned to the nature of the activating agent used during
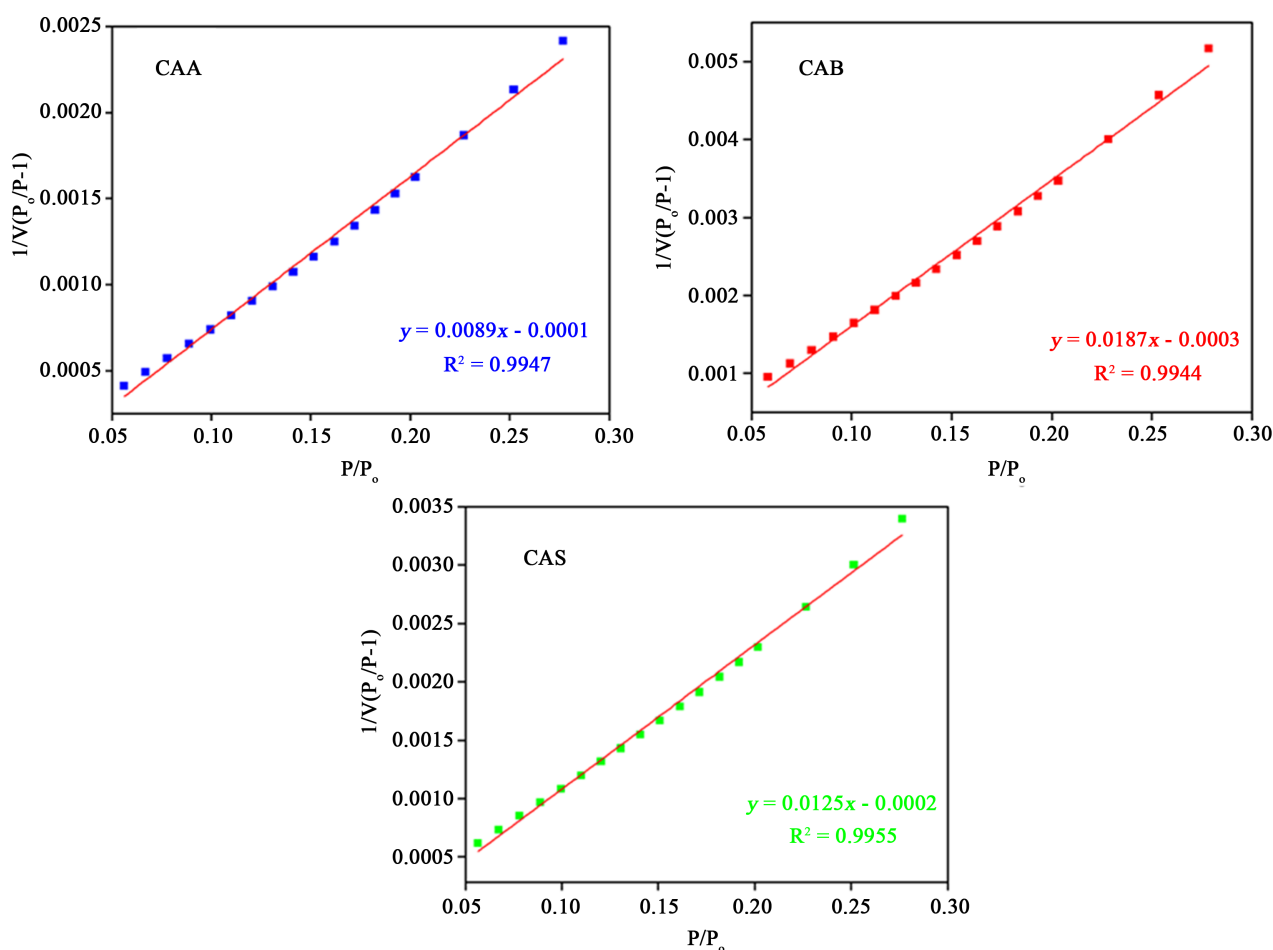
Figure 6. Linear representation of BET equation for CAA, CAB and CAS.

the chemical activation. The decreasing order of the BET specific surfaces area of the different carbons (CAA > CAS > CAB) was in good accordance with those found in acetic acid and methylene blue adsorption studies. In view of the results obtained for surface area determination, BET method seems to be the best one indicated for the determination of the specific surface of a porous solid. These results once again confirm the iodine indices obtained (Figure 7).

The nitrogen adsorption isotherms also give information about pore volume and pore diameter (Table 4). The pore size distribution is calculated according to Barrett, Joyner and Halenda method [45] also called BJH method. Figure 8 shows pore diameter distribution of each prepared activated carbon. Pore size can be described by its width (for slit-like pores), that means the average distance between two opposite walls, or by its diameter. According to the classification recommended by IUPAC [46], there are three groups of pores according to their size: micropores (size < 20 Å), mesopores (size between 20 Å and 500 Å), macropores, (size > 500 Å). However, the thresholds between the different categories are not really so well defined, as their determination depends particularly on the shape of the pore. BJH pore size distribution curves show peaks ranging from 10 to 50 Å, with a maximum at around 11.26 Å for CAA, 11.78 Å for CAB and 11.77 Å for CAS. This result indicates the presence of micropores and mesopores in the three adsorbents. However, micropores appear to be predominant in activated carbons independently to the activating agent. Since the adsorption capacity of activated carbons is the most important property directly related to the specific surface area and pore volume [47] and according to BET analysis, CAA seems better among the three carbons prepared.

SEM images were obtained from the Department of Chemical Engineering, Laval University, Quebec, Canada. The sample of activated carbons was observed under three different magnifications which are displayed in Figure 9. The surface morphologies of the prepared materials are quite different, despite
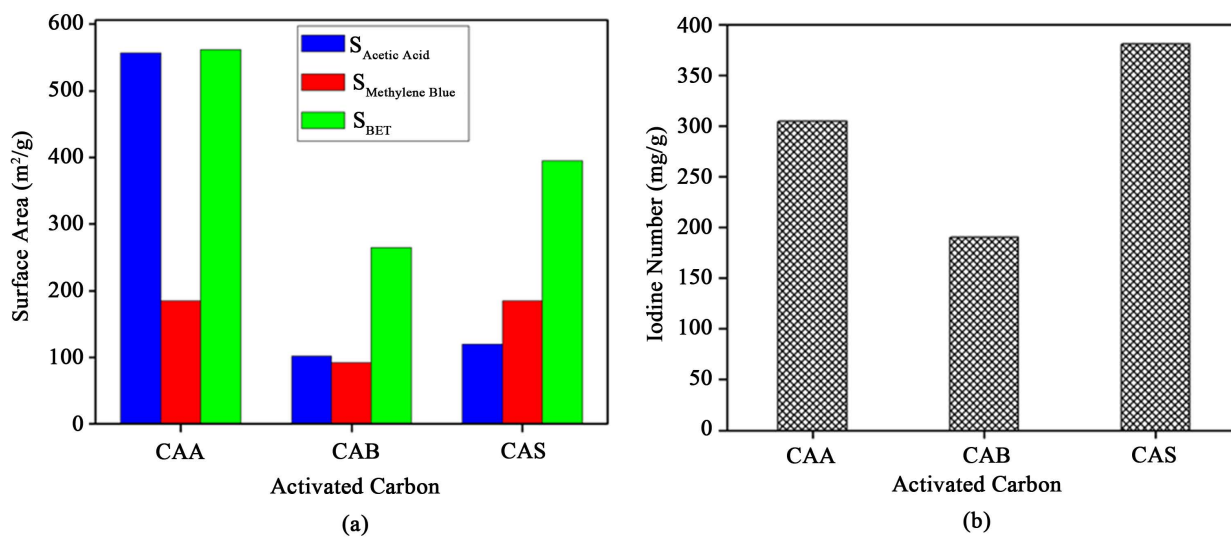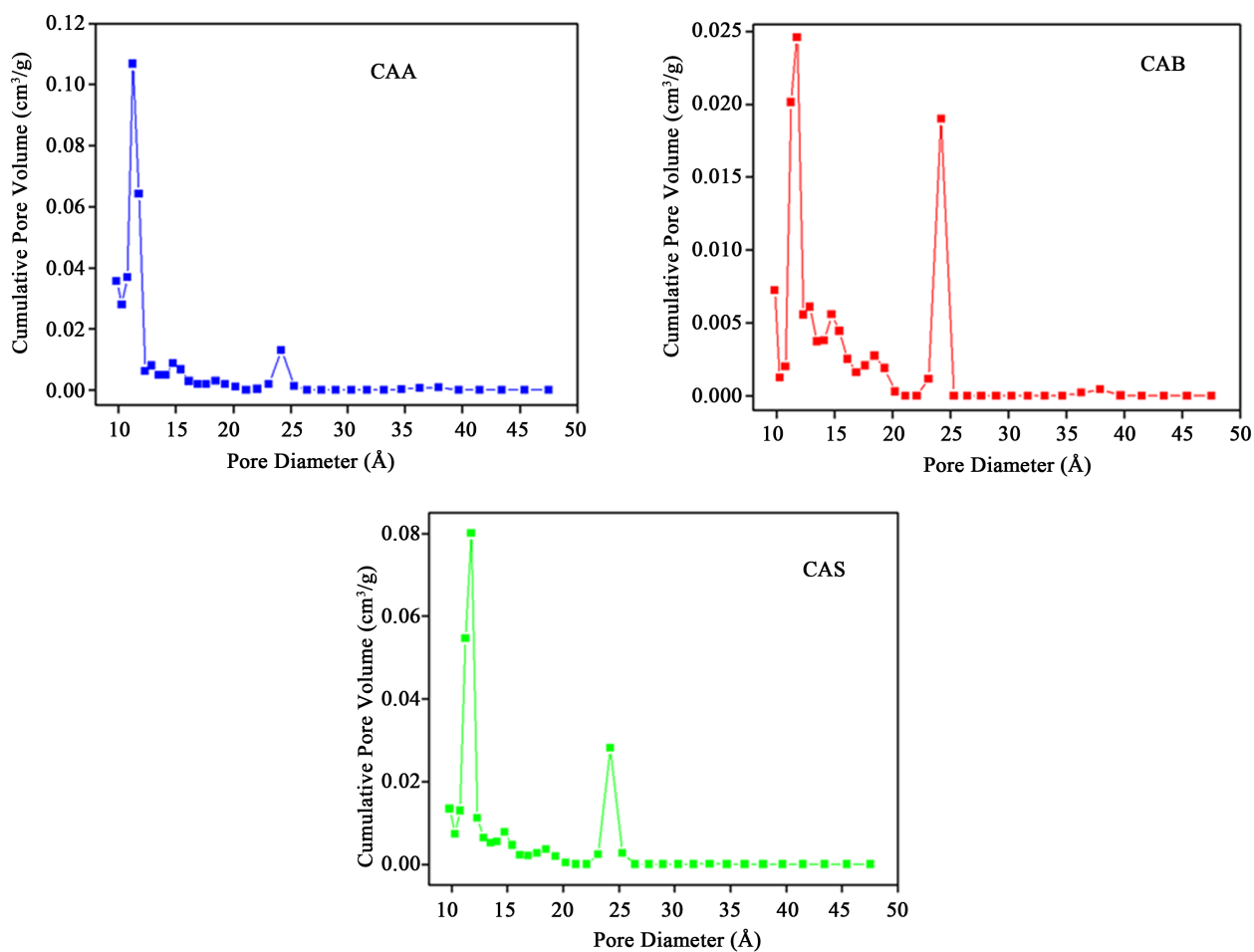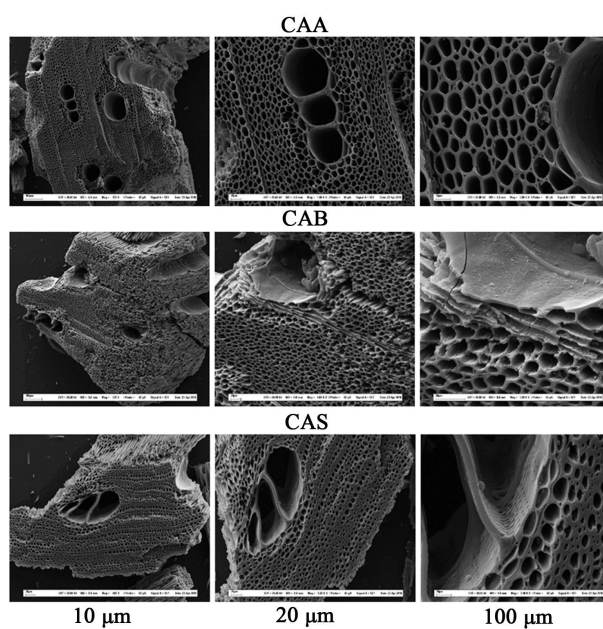

Figure 7. Effect of activation agent on (a) surface area and (b) iodine number.

Figure 8. Pore diameter distribution of CAA, CAB and CAS.

Figure 9. SEM images of CAA, CAB and CAS at different magnifications (10 μm, 20 μm and 100 μm).

the fact that all are from the same biomass. The difference in texture between CAA, CAB and CAS could be assigned to the type of activating agent used during their synthesis. These observations once more indicate that the activating agent has some effects during the activation and thus on pore creation.

4. Conclusions

A set of activated carbons from local material (*Acacia auriculeaformis*) chemical activated with H_3PO_4 acid, NaOH base and NaCl salt were prepared and characterized. As compared to the three methods (AC, BM and BET) used for surface area determination, it was found that BET method gives the best results. Thus, the prepared activated carbons have specific surface areas ranging from 265.00 to 561.60 m^2/g and pore volumes from 0.13 to 0.26 cm^3/g. These specific surface areas confirm the orders of adsorption capacity of iodine ranging from 190.35 to 380.71 mg/g. The chemical activation of this material has provided active microporous sites (isothermal type I). Boehm chemical analysis and the determination of zero point charge pH showed the presence of various functional groups on the surface of the activated carbons and some uniformities between the pH_{ZPC} values and the proportions in acidic and basic functional groups. At the end of this work, it is clear that carbon from *Acacia auriculeaformis* activated with phosphoric acid seems better than the two others as it provides high yield (41.81%), low ash rate (5%), high specific surface area (561.60 m^2/g) and large pore volume (0.26 cm^3/g). However, the next work will be devoted to the study of the adsorptive capacity of this carbon in the removal of various metallic pollutants in order to evaluate its effectiveness in water treatment.

Acknowledgements

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Hecini, L. and Achour, S. (2014) Coagulation-floculation au sulfate d'aluminium de composés organiques phénoliques et effet de sels de calcium et de magnésium. *Revue des Sciences de l'Eau*, **27**, 271-280. https://doi.org/10.7202/1027810ar

[2] Lamia, A., Jihane, C., Abdelkarim, C. and Amina, B. (2009) Traitement biologique des eaux usées textiles-Étude de cas: Station d'épuration des eaux usées textiles. *European Journal of Water Quality*, **14**, 27-37. https://doi.org/10.1051/asees/2009005

[3] Zaviska, F. (2011) Modélisation du traitement de micropolluants organiques par oxydation électrochimique. Thèse, Québec, Université du Québec, Institut national de la recherche scientifique, Doctorat en Sciences de l'Eau, 385.

[4] Trabelsi, S. (2011) Etudes de traitement des lixiviats des déchets urbains par les procédés d'oxydation avancée photochimiques et électrochimiques: Application aux lixiviats de la décharge tunisienne "Jebel Chakir". Sciences de la Terre, Doctorat Université Paris-Est, Français.

[5] Brahima, S., Patrick, D., Géraldo, B., Jean, F.B. and Marc, H. (2011) État actuel des connaissances des procédés de bioréacteur à membrane pour le traitement et la réutilisation des eaux usées industrielles et urbaines. *Revue des Sciences de l'Eau*, **24**, 283-310. https://doi.org/10.7202/1006478ar

[6] Meçabih, Z., Kacimi, S. and Bouchikhi, B. (2006) Adsorption des matières organiques des eaux usées urbaines sur la bentonite modifiée par Fe (III), Al (III) et Cu (II). *Revue des Sciences de l'Eau*, **19**, 23-31. https://doi.org/10.7202/012261ar

[7] Sakr, F., Sennaoui, A., Elouardi, M., Tamimi, M. and Assabbane, A. (2015) Étude de l'adsorption du Bleu de Méthylène sur un biomatériau à base de Cactus. *Journal of Materials and Environmental Science*, **6**, 397-406.

[8] Danish, M., Hashim, R., Ibrahim, M.N.M., Rafatullah, M., *et al.* (2011) Characterization of Acacia Mangium Wood Activated Carbons Prepared in the Presence of Basic Activating Agents. *BioRessourses*, **6**, 3019-3033.

[9] Shen, Y.S., Wanga, S.L., Tzou, Y.M., Yan, Y.Y.I. and Kuan, W.H. (2012) Removal of Hexavalent Cr by Coconut Coir and Derived Chars—The Effect of Surface Functionality. *Bioresource Technology*, **104**, 165-172.
https://doi.org/10.1016/j.biortech.2011.10.096

[10] Basta, A.H., Fierro, V., Saied, H. and Celzard, A. (2011) Effect of Deashing Rice Straws on Their Derived Activated Carbons Produced by Phosphoric Acid Activation. *Biomass and Bioenergy*, **35**, 1954-1959.
https://doi.org/10.1016/j.biombioe.2011.01.043

[11] Balogoun, C.K., Bawa, M.L., Osseni, S. and Aina, M. (2015) Préparation des charbons actifs par voie chimique à l'acide phosphorique à base de coque de noix de coco. *International Journal of Biological and Chemical Sciences*, **9**, 563-580.
https://doi.org/10.4314/ijbcs.v9i1.48

[12] Gbamele, K.S., Atheba, G.P., Dongui, B.K., Drogui, P., Didier, R. and Kra, D.O. (2016) Contribution à l'étude de quatre charbons activés à partir des coques de noix de coco. *Afrique Science*, **12**, 229-245.

[13] Bossombra, K.V., Tchirioua, E., Ekou, L. and Trong-On, D. (2018) Nitrogen Enrichment of Activated Carbon Made from Coconut Shell of Ivory Coast and Its Application in Cd^{2+} Ions Removal. *Australian Journal of Basic and Applied Sciences*, **12**, 38-44.

[14] Sahu, J.N., Acharya, J. and Meikap, B.C. (2010) Optimization of Production Conditions for Activated Carbons from *Tamarind wood* by Zinc Chloride Using Response Surface Methodology. *Bioresource Technology*, **101**, 1974-1982.
https://doi.org/10.1016/j.biortech.2009.10.031

[15] Nko'o Abuiboto, M.C., Avom, J. and Mpon, R. (2016) Évaluation des propriétés de charbons actifs de résidus de Moabi (*Baillonella toxisperma* Pierre) par adsorption d'iode en solution aqueuse. *Revue des sciences de l'eau*, **29**, 51-60.
https://doi.org/10.7202/1035716ar

[16] Lyubchik, S.B., Benaddi, H., Shapranov, V.V. and Beguin, F. (1997) Activated Carbons from Chemically Treated Anthracite. *Carbon*, **35**, 162-165.
https://doi.org/10.1016/S0008-6223(97)81121-9

[17] Romero-Anaya, A., Ouzzine, M., Lillo-Rodenas, M. and Linares-Solano, A. (2014)

Spherical Carbons: Synthesis, Characterization and Activation Processes. *Carbon*, **68**, 296-307. https://doi.org/10.1016/j.carbon.2013.11.006

[18] Verla, A., Horsfall, M., Verla, E., Spiff, A. and Ekpete, O. (2012) Preparation and Characterization of Activated Carbon from Fluted Pumpkin (*Telfairiaoccidentalis Hook.F*) Seed Shell. *Asian Journal of Natural & Applied Sciences*, **1**, 39-50.

[19] Dolasa, H., Sahinb, O., Sakac, C. and Demirb, H. (2011) A New Method on Producing High Surface Area Activated Carbon: The Effect of Salton the Surface Area and the Pore Size Distribution of Activated Carbon Prepared from Pistachio Shell. *Chemical Engineering Journal*, **166**, 191-197.
https://doi.org/10.1016/j.cej.2010.10.061

[20] Tchakala, I., Bawa, L.M., Djaneye-Boundjou, G., Doni, K.S., Nambo, P. (2012) Optimisation du procédé de préparation des Charbons Actifs par voie chimique (H_3PO_4) à partir des tourteaux de Karité et des tourteaux de Coton. *International Journal of Biological and Chemical Sciences*, **6**, 461-478.
https://doi.org/10.4314/ijbcs.v6i1.42

[21] Altenor, S., Carene, B., Emmanuel, E., Lambert, J., Ehrhardt, J.-J. and Gaspard, S. (2009) Adsorption Studies of Methylene Blue and Phenol onto Vetiver Roots Activated Carbon Prepared by Chemical Activation. *Journal of Hazardous Materials*, **165**, 1029-1039. https://doi.org/10.1016/j.jhazmat.2008.10.133

[22] Kra, D.O., Kouadio, N.A., Atheba, G.P., Coulibaly, B., Allou, N.B., Gbassi, K.G. and Trokourey, A. (2015) Modélisation des propriétés adsorbantes de charbons activés issus de deux variétés d'acacia (*auriculiformis et mangium*). *International Journal Of Innovation and Scientific Research*, **13**, 542-553.

[23] Mezerette, C. and Vergnet, L.F. (1994) La voie thermochimique. In: *ANONYME-Guide Biomasse Energie*, Collection études et filières. 144-198.

[24] Honoré, P., Kouakou, U., Dembele, A., Yapo, A.J. and Trokourey, A. (2014) Preparation and Characterization of Activated Carbons Based on Peanut Shell (*Arachis hypogaea*) Green Soya Shell (*Vigna radiata*). *International Journal of Science and Research*, **3**, 933-937.

[25] Gueye, M. (2015) Développement de charbon actif à partir de biomasses ligno-cellulosiques pour des applications dans le traitement de l'eau. Thèse, Institut International de l'ingénierie de l'Eau et l'Environnement (2iE), Ouaga/B. Faso.

[26] Ousmaila, S.M., Adamou, Z. and Ibrahim, D. (2016) Préparation et caractérisation de charbons actifs à base de coques de noyaux de Balanites Eagyptiaca et de Zizyphus Mauritiana. *Journal de la Société Ouest-Africaine de Chimie*, **41**, 59-67.

[27] Boehm, H. (1966) Chemical Identification of Surface Groups. In: *Advances in Catalysis*, Academic Press, London, 179-274.
https://doi.org/10.1016/S0360-0564(08)60354-5

[28] Bamba, D. (2007) Elimination du diuron des eaux par des techniques utilisant les ressources naturelles de Cote d'ivoire: Photocatalyse solaire et charbons actifs de noix de coco. Thèse de Doctorat des Universités de Cocody-Abidjan et de Metz.

[29] Vasu, A.E. (2008) Surface Modification of Activated Carbon for Enhancement of Nickel (II) Adsorption. *E-Journal of Chemistry*, **5**, 814-819.
https://doi.org/10.1155/2008/610503

[30] Avom, J., Ketcha, M., Matip, M. and Germain, P. (2001) Adsorption de l'acide acétique par des charbons d'origine végétale. *African Journal of Science and Technology, Science and Engineering*, **2**, 1-7. https://doi.org/10.4314/ajst.v2i2.44663

[31] Kifuani, K.M.A., Noki, V.P., Ndelo, D.P.J., Mukana, W.M.D. and Ekoko, B.G.

(2012) Adsorption de la quinine bichlorhydrate sur un charbon actif peu coûteux à base de la Bagasse de canne à sucre imprégnée de l'acide phosphorique. *International Journal of Biological and Chemical Sciences*, **6**, 1337-1359. https://doi.org/10.4314/ijbcs.v6i3.36

[32] Brunauer, S., Emmett, P.H. and Teller, E. (1938) Adsorption of Gases in Multimolecular Layers. *Journal of the American Chemical Society*, **60**, 309-319. https://doi.org/10.1021/ja01269a023

[33] Tatianne, F.D.O. (2011) Étude d'un procédé de dépollution basé sur le couplage ozone/charbon actif pour l'élimination des phtalates en phase aqueuse. Alimentation et Nutrition,Université d'Orléans, Français.

[34] Haimour, N.M. and Emeish, S. (2006) Utilization of Date Stones for Production of Activated Carbon Using Phosphoric Acid. *Waste Management*, **26**, 651-660. https://doi.org/10.1016/j.wasman.2005.08.004

[35] Linares, S., Angel, L., Maria, M.L., Juan, K. and Mirko, R.A. (2012) NaOH and KOH for Preparing Activated Carbons Used in Energy and Environmental Applications. *International Journal of Energy, Environment and Economics*, **20**, 59-91.

[36] Ayvral, C. (2009) Elimination des polluants aromatiques par oxydation catalytique sur charbon actif. Thèse de Doctorat, Université de Toulouse.

[37] Gueu, S. (2007) Traitement de la pollution métallique et organique par les charbons actifs des coques de noix de coco et des graines de palmiste. Thèse de Doctorat de 3eme cycle, Université de Cocody.

[38] Silex International Charbon actif haut qualité, T2, Activ' OG8*30. http://www.silexinternational.com/

[39] Wibowo, N., Setyadhi, L., Wibowo, D., Setiawan, J. and Ismadji, S. (2007) Adsorption of Benzene and Toluene from Aqueous Solutions onto Activated Carbon and Its Acid and Heat Treated Forms: Influence of Surface Chemistry on Adsorption. *Journal of Hazardous Materials*, **146**, 237-242. https://doi.org/10.1016/j.jhazmat.2006.12.011

[40] Atheba, G.P., Allou, N.B., Dongui, B.K., Kra, D.O., Gbassi, K.G. and Trokourey, A. (2015) Butyl Paraben Adsorption on Coal-Based on Low-Coast of Coconut Shells from Côte d'ivoire. *Innovative Space of Scientific Research Journals*, **13**, 530-541.

[41] Canizares, P., Carmona, M., Baraza, O. and Delgado, A. (2006) Adsorption Equilibrium of Phenol onto Chemically Modified Activated Carbon F400. *Journal of Hazardous Materials*, **131**, 243-248. https://doi.org/10.1016/j.jhazmat.2005.09.037

[42] Khelifi, A., Temdrara, L. and Addoun, A. (2009) Effet de la texture poreuse et de la structure chimique sur l'adsorption du bleu de méthylène par des charbons actifs oxydés. *Journal de Société Algérienne de Chimie*, **19**, 13-25.

[43] Daoud, M. and Benturki, O., (2014) Activation d'un charbon à base de noyaux de jujubes et application à l'environnement. Adsorption d'un colorant de textile. *Revue des Energies Renouvelables*, **14**, 155-162.

[44] Khezami, L. and Capart, R. (2005) Removal of Chromium (VI) from Aqueous Solution by Activated Carbons: Kinetic and Equilibrium Studies. *Journal of Hazardous Materials*, **123**, 223-231. https://doi.org/10.1016/j.jhazmat.2005.04.012

[45] Barrett, E.P., Joyner, L.G. and Halenda, P.P. (1951) The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms. *Journal of the American Chemical Society*, **73**, 373-380. https://doi.org/10.1021/ja01145a126

[46] Atheba, P., Gbassi, G.K., Dongui, B., Bamba, D., Yolou, F.S. and Trokourey, A.

(2014) Études de la porosité, de la surface spécifique et des fonctions de surface de charbons actifs préparés après carbonisation artisanale des coques de noix de coc. *Les technologies de laboratoire*, **8**, 126-136.

[47] Nowicki, P., Pietrzak, R. and Wachowska, H. (2010) Sorption Properties of Active Carbons Obtained from Walnut Shells by Chemical and Physical Activation. *Catalysis Today*, **150**, 107-114. https://doi.org/10.1016/j.cattod.2009.11.009