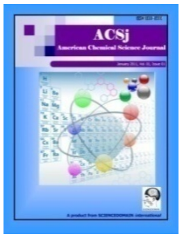

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Preparation and Characterization of Activated Carbons Obtained from Maize Cobs by Zinc Chloride Activation

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Authors' contributions

This work was carried out in collaboration between all authors. Author DJDD designed the study, wrote the first draft and managed the literature searches. Authors JMK and HMN managed all the analysis of the study and corrected the first manuscript. Author NJN also corrected the manuscript. All authors read and approved the final manuscript.

Research Article

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ABSTRACT

Aims: To set up high adsorbent materials at lower cost from agricultural wastes in this case maize cobs and to characterize these materials.
Study Design: Determination of the textural and physicochemical properties of the prepared materials.
Place and Duration of Study: Technological University of Chalmers, Nuclear Chemistry Laboratory, Goteborg, Sweden, between November 2010 and January 2011.
Methodology: Five activated carbon samples of maize cobs were prepared by chemical activation with zinc chloride ($ZnCl_2$). They were characterized and the values of their textural (SEM images and XRD patterns) and physicochemical properties (specific surface area, pore volume, pore size and functional groups) were determined and compared with those of a commercial activated carbon of animal origin.
Results: The results showed that the part of the cob used, the residence time, the quantity and the state of the activating agent affected the activated carbon produced. Thus, the carbon material obtained from the woody belt (hard part of the cob) showed the most significant properties with a specific surface area of 701.68 m^2/g and a porous volume of

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about 0.39 cm^3/g. On the other hand, samples obtained from the soft part of the cob mixed with small particles of woody belt, gave low specific surface area (0.43-11.62 m^2/g) and porous volumes (0.00028-0.11 cm^3/g). In addition, all these chars presented acidic functions at their surfaces.

Conclusion: The study revealed that maize cobs particularly the hard part of the cobs, an agricultural waste, can be used as raw material for the preparation of activated carbon.

Keywords: Activated carbon; maize cobs; chemical activation; physicochemical properties.

1. INTRODUCTION

Human activity is at the origin of immense environmental degradation as seen through widespread contamination and pollution. Well known and frequently used techniques for elimination of wastes from gas and liquid streams include oxidation, precipitations, filtrations, ions exchange, ultra filtration, reverse osmosis, electrochemical deposits and adsorption (Lallemand-Barrès, 2000; Masclet, 2005; Meunier and Liang-Ming, 2003) on the compounds such as zeolites, clays, silica gel, the resins, alumina activated or the activated carbon are found in literature (Meunier and Liang-Ming, 2003; Thibault-Starzyk, 2004). Most of these techniques are not achievable in very expensive, small and medium-size companies hence the need to choose technologies which are simple, economic, effective and, especially non-polluting such as adsorption (Meunier and Liang-Ming, 2003; Thibault-Starzyk, 2004). Thus, adsorption with porous surfaces has frequently being used for the elimination of contaminants found at low concentrations in the environment and in the industrial effluents.

In view of the above, a diversity of adsorbent materials has been tested for their suitability in the elimination of contaminants. Activated carbons turned out to be the most used, not only because of its high adsorptive capacity (Kadirvelu et al., 2003; Marsh and Rodriguez-Reinoso, 2006; Sircar et al., 1996) and its intrinsic physicochemical properties such as porosity, specific surface area and the nature of surfaces, but also because of the abundance of raw material from which it can be prepared. Activated carbon is used in several industrial applications; in the extraction of organic and inorganic pollutants found in aqueous or in gas phase, water and waste water treatment, metal extraction, sugarcane juice decolourization, in the pharmaceutical and agro based industrial waste (Lynch, 2001; Marsh and Rodriguez-Reinoso, 2006; Van der Hoek, 1999; Wrench, 2007).

The activated carbons, distinguishable by their conditions of preparation, and consequent characteristics were prepared from maize cobs; a raw material which had not been used before in our lab. The preference for maize cobs is due to several reasons. Maize, the raw material chosen for this study, is widely grown in Cameroon and in the central African sub-region. Reason for the choice of maize cobs is twofold; availability and thermodynamics factor. In most cases, the residues from the primary processing of maize, which consists of foliage, stalks and cobs, except in the arid Sahel North of the country where they are used as fuels for domestic heating or for cattle nutrition, are usually disposed in the open air. Thus, a huge amount of maize cobs are harvestable for the preparation of activated carbon. Secondly, on purely thermodynamic considerations, maize cob has a low combustion energy value and, thus, a low carbonization temperature compared to other biomass residues (Zych, 2008).

Through the years, activated carbon has been prepared by two stage process involving chemical activation. That is the impregnation of the carbonaceous material with a chemical species-usually an inorganic salt-followed by carbonization. The challenge has been first, the search for suitable chemical species for impregnation and, second, determining the most appropriate operating carbonization conditions that will favour the production of the most desirable properties per surface area in the activated carbon. Whereas carbonization removes volatile matters from the raw material, activation serves to develop the porosity of the material in the course of the carbonization. The carbonization process is very energy dependent and constitutes a significant cost component in industrial production. Therefore, a raw material such as maize cob, requiring lower carbonization is preferable to other biomass.

Usually, carbonization and activation take place separately and several authors such as Chilton et al. (2003) and Koutcheiko et al. (2007) have adopted that strategy. Recently, the tendency has been, rather, to prepare the activated carbon resulting from agricultural wastes by chemical activation (carbonization and activation simultaneously) (Adinata et al., 2007; Avom, 1982; Avom et al., 2001; Boudrahem et al., 2009; Ibañez, 2002). The development of the pores during the preparation is very difficult to observe and the majority of the authors such as Tang and Bacon (1964) and Soltes and Elder (1981) were limited like in this work to the interpretation of the phenomena observed during the preparation such as the releases of gas and the liquids rejected by this preparation according to time and of the temperature.

Temperature is known to be a determinant factor in the activated carbon structure produced. Carbonization which takes place at low temperatures, generally, gives a material having low porosity (Avom, 1982; Avom et al., 2001) and a disordered structure, whereas the activation which takes place at high temperatures develop porosity (Avom, 1982; Avom et al., 2001). Literature on the preparation of activated carbon from diverse sources, particularly agricultural residues, under different experimental conditions and methods are abundant (Acharya et al., 1999; Cronje et al., 2002; Kumar et al., 2010; Rastogi et al., 2007; Sahu et al., 2009). Usually, such studies have involved the comparison of the performance of the ensuing activated carbon with a commercial activated carbon with respect to the elimination of ions at low concentration. Results reveal some lack of correlation between carbonization temperature and its duration, and between chemical species loading to well known factors as porosity, site pore concentration, adsorptive capacity etc (Lazano-Castello et al., 2001). Data on preparation of activated carbon from maize cobs, even with the widespread use of maize is not known to enable the exploitation of its residue for industrial scale preparation.

The innovation of this work resides not only on the raw material the maize cobs of Cameroon, but also in the mode of obtaining the activated carbon. Indeed in former work on the preparation of the activated carbon from maize cobs (Chang et al., 2000; Tsai et al., 1998; Tsai et al., 2001), the cobs were directly mixed with the precursor whereas in this work, the activated carbon are obtained starting from the various parts of the cobs (the hard part and the soft part). In addition, the activating agent (zinc chloride) was used in solution and in solid state which is an innovation because the majority of the authors in the same line for the preparation of AC (Boudrahem et al., 2009; Tsai et al., 1998) used zinc chloride only in the liquid state. In addition contrary to the authors such as Qiang et al. (2007) whose aims are to obtain materials with very significant porosity characters, this work, in teals and improvement in chemical properties like surface functional groups. These activated carbons are designed to improve environment and hygienic status in Cameroon where there are pollution problems mainly water pollution.

The objective of this work was to prepare and characterize activated carbon from maize cobs in order to relate the preparation conditions (carbonization and chemical activation) to the carbon's essential physicochemical properties. The chemical species used here was zinc chloride. Thus, in this work, powder samples of maize cobs with different $ZnCl_2$ loading will be subjected to carbonization at different time duration. Carbonization and activation will be carried out simultaneously.

2. EXPERIMENTAL DETAILS

2.1 Preparation of Activated Carbon from Maize Cobs

The maize cob is, structurally, made up of two distinct parts—the soft part consisting of the periphery and marrow; the woody belt which constitutes the hard part of the cob.

2.1.1 Crushing and separation into different particle sizes

The maize cobs used in this work came from a field located at SOA, a University town located about 10 km from Yaoundé, the capital of Cameroon. Upon harvesting, the maize cobs contained several impurities, particularly earth. It was thus necessary to wash them abundantly to get rid of all the impurities which could influence the final composition of material. The washing was followed by drying for a long period open air in order to remove the residual water from washing as well as to reduce the moisture content of the fresh cobs. They were then crushed and sieved (sieve type; AFNOR X11-501) and then distributed in a distributor of the type RETSCH and then they were crushing into different particle sizes. The finest particles resulted from the soft part of the cob and largest of the hard part. The distributor distributed the raw material particles in definite intervals of sizes while separating those particles not within the desired interval. The particles were divided into two parts according to their particle sizes. One part was primarily made up of the soft part of the cobs (periphery and marrow) and fine particles of the hard part (thicknesses ranging between 1.25 and 1.75 mm). The other part was made up, exclusively, of the hard part of the cobs (woody part) having particle sizes higher than 1.75 mm. The two parts were visible not only by the physical appearance (left soft and part lasts) and also by the colour (the soft part was gray and white and the hard part was ox-blood coloured). Thus the soft parts with some hard particles passed in first through the sieve while the hard parts recognizable by their appearance and colour were retained on the sieve.

2.1.2 Chemical activation with zinc chloride salt

After obtaining the crushed particles, they were separated into the following 5 samples labelled on the basis of the concentration or state of the activation salt and the activation time M10-60-100, M10-24-100, MAPZC3, MAPZC4 and MAPZC5. Thus, the first two samples, M10-60-100 and M10-24-100, activated by use of a 10% solution of ZnCl2 and for duration of 60 minutes (one hour) and 24 hours, respectively. The samples labelled MAPZC3, MAPZC4 and MAPZC5 were activated with solid $ZnCl_2$ (2g, 3g and 1g respectively) for 60 minutes (Table 1).

To activate a sample, the following procedure was carried out. The crushed particles (20g) were weighed on an electronic balance with high sensitivity. The material was dried in a desiccators to remove the high initial moisture content before transferring to a drying oven set at 120ºC for 24 hours. After 24 hours it was assumed that all the moisture and some of the volatile material had left. The material was then re-dried in the desiccator and weighed once again. It was then impregnated with the activating agent (zinc chloride). According to the sample, the activating agent was mixed with the matter by agitating for one hour to ensure the access of $ZnCl_2$ to the interior of the precursor until a homogeneous mixture is obtained. The impregnation ratios and the state of the activating agent are found in Table 1. After the impregnation the mixture (raw material and activating agent) was returned to the oven for 24 hours. A dried mixture ready to be carbonized was thus obtained.

Table 1. Mode of preparation of the activated carbon of maize cobs by $ZnCl_2$ activation

Adsorbent	**[a]M10-60-100**	**[b]M10-24-100**	**[c]MAPZC3**	**[d]MAPZC4**	**[e]MAPZC5**
Particles size (mm)	1.25-1.75	1.25-1.75	1.25-1.75	1.25-1.75	≥1.75
Concentration (%) or masses of activating agent (g)	10%	10%	2	3	1
Impregnation ratio ($w_{ZnCl2}/w_{maize\ cobs}$)	1/200	1/200	1/10	3/20	1/20
Residence time (h)	1	24	1	1	1
Mass of obtained material on the outlet side of the furnace (g)	5.312	4.9839	7.2157	10.1365	7.6081
Mass of activated carbon after washing and drying (g)	5.284	4.8613	6.0252	8.5830	7.1270
Physical aspect of the activated carbon obtained	soft and black seeds	soft and black seeds	Black seeds	Black seeds	Large black seeds

[a]M10-60-100: Maize cobs activated carbon (light part) obtained with 10%$ZnCl_2$ solution and time residence=60minutes; [b]M10-24-100: Maize cobs (light part) activated carbon obtained with 10% $ZnCl_2$ solution and time residence=24 hours; [c]MAPZC3: Maize cobs (light part) activated carbon obtained with 2g of solid $ZnCl_2$; [d]MAPZC4: Maize cobs (light part) activated carbon obtained with 3g of solid $ZnCl_2$; [e]MAPZC5: Maize cobs activated carbon (hard part) obtained with 1g of solid $ZnCl_2$. Operating conditions: Impregnation duration: 1hour; heating rate: 10ºC/min; Carbonization temperature: 500ºC; temperature of cooling: 100ºC.

2.1.3 Carbonization

The experimental set up for carbonization is shown in Fig. 1. This experimental device consisted of a continuous steel pipe (F) of type AVANTEC model 92884 which can reach a temperature of 1200ºC and having a device regulating the temperature according to time (T), of a quartz tube (Q) having an opening (A) in which the mixture (M) obtained previously was introduced for carbonization using a spatula. The Pyrex tube (P) having two openings of which one was connected to the quartz tube (Q) in (A) this supplements experimental set up. The purpose of this tube provided with a valve (V) was to control the exit of gases. Carbonization in itself consisted of the introduction into the quartz tube (Q) of the mixture (M). The tube (Q) was then introduced into the furnace (F) heated beforehand at 100ºC. The speed of heating (regulated on the level of (T)) was maintained at 10ºC/min. The duration of impregnation was maintained at 1 hour and the maximum temperature at 500ºC for all the samples.

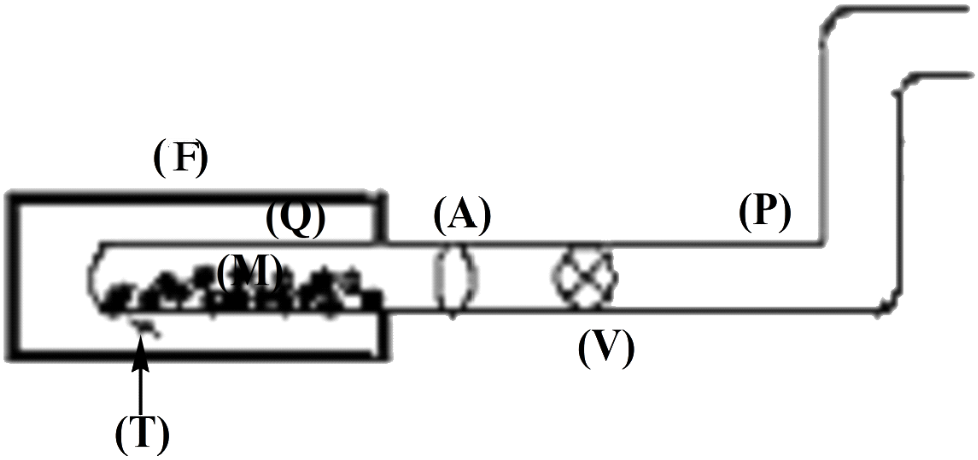


Fig. 1. Experimental set up in the preparation of the activated carbon of maize cobs
(F): Continuous steel pipe; (T): Temperature regulator; (Q): Quartz tube; (A): Opening; (M): Mixture; (P): Pyrex tube; (V): Valve.

Around 200ºC, very intense white vapours were observed. From 250ºC, on the walls of the two tubes a yellow liquid of oily aspect of which the quantity increased as the temperature goes up was also observed. The vapours became less intense around 500ºC except for the MAPZC5 sample where the vapours remained quite intense around 500ºC and disappeared completely only 30 minutes after having reached this temperature. The valve (V) was opened from time to time according to the intensity of gases of decomposition in the quartz tube (Q) to evacuate gases. After having reached 500ºC, no gaseous emission was observed. Carbonization was stopped. The device (T) of the furnace was regulated so that the temperature goes down until 100ºC. The material then left the furnace was introduced into a flask and then weighed.

The materials were thoroughly washed in a flask by filtration with distilled water and soaked in 1% hydrochloric acid solution for 2 h in order to eliminate the residual zinc from the pores of the carbons. The materials were washed again with hot distilled water and finally cold water. Then they were dried in the oven at 120ºC and then reweighted (results in Table 1). The various operational conditions for the preparation of the various activated carbon samples are summarized in Table 1. The different stages of preparation of the activated carbon from maize cobs are clearly summarized in Fig. 2. For purposes of comparison, a commercial powdered activated carbon sample labelled OA00 (animal origin (OA) without any treatment (00)) and obtained from PROLABO, RHÔNE-POULENC, Nº 22614 was used.

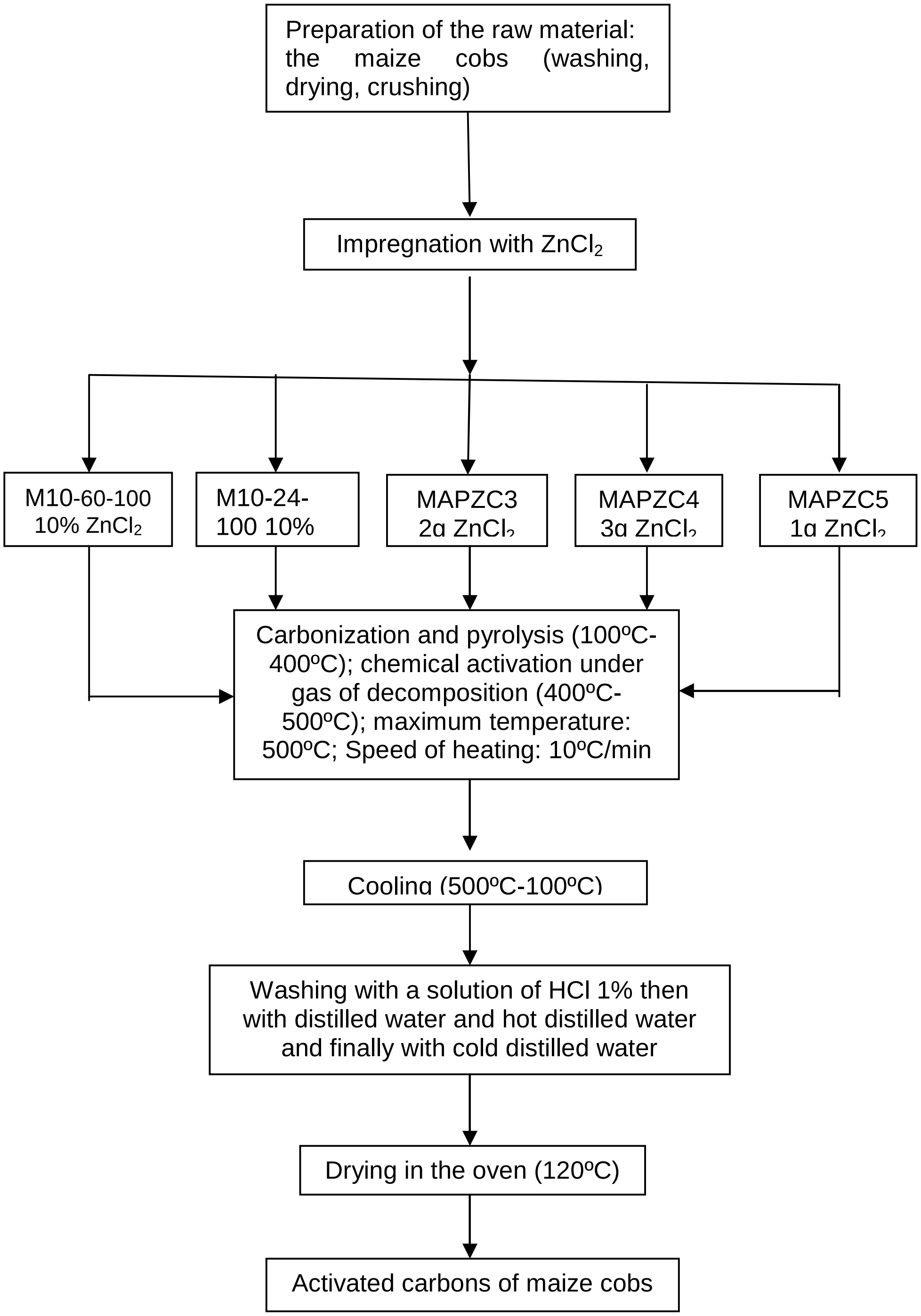


Fig. 2. General Scheme for the preparation of the activated carbon of Crop origin
(in this case, maize cob)

2.2 Characterizations Techniques

Four techniques of characterization have been used to characterize the activated carbons of maize cobs according to the furnished information's (structure, chemistry, morphology and porosity (Crini and Badot, 2007; Dresselhaus et al., 1992).

2.2.1 SEM-EDX analysis

Characterization was performed by electron microscopy with EDX detection for the determination of relevant elements using a FEI Quanta 200 FEG (Field Emission Gun) ESEM operated at 15-20 kV and coupled to an Oxford Inca 300 EDX system. The detection limit of EDX-system was about 1 wt% and the penetration depth was about 1 µm. The micrographs of the activated carbon of maize cobs (size 20 µm) and of sample OA00 (size 2 µm) provided by the SEM and the elementary chemical compositions are found in the third part.

2.2.2 XRD analysis

The main crystalline compounds in samples were identified by qualitative X-ray powder diffractometry (XRD) using a Siemens D5000 X-ray powder diffractometer with the characteristic copper radiation and a scintillation detector. The identification of compounds was performed through comparison with standards in the Joint Committee of Powder Diffraction Standards issue 2010 (IUPAC, (2010)). XRD patterns of the studied activated carbons are found in the third part.

2.2.3 FTIR analysis

The Fourier transform Infra red (FTIR) analysis of maize cobs was carried out by a FTIR equipment of mark SPECTRUM ONE FT-IR incorporated with software (Perkin Elmer Instruments version 3.02.01) for the examination of the spectra. For sample analysis, 0.5 g of activated carbon was mixed with about the same amount of potassium bromide KBr. The mixture thus obtained was crushed in a mortar to obtain a homogeneous powder which was then introduced into a mould to obtain very fine plates. The plates were then introduced into the spectrophotometer for analysis. The wave number was found to vary between 4000 and 450 cm^{-1}. FTIR spectra of the studied activated carbon are found in the third part.

2.2.4 Specific surface area and porosity

Specific surfaces area and porosity were determined by physical adsorption of nitrogen N_2 on the surface of the activated carbon. Nitrogen adsorption measurements were carried out with an ASAP 2020 instrument from Micromeritics, USA. This equipment measured automatically, the adsorption and desorption isotherms at T=77 K and from the data, it calculated a Brunauer-Emmett-Teller (BET) model fitting for specific surface area. The porosity included total volume and surface area of mesopores and lower range of macropores (measurable size range: 2-300Å) were also measured.

Before the analyses, samples of about 0.1 g were degassed at vacuum (about 5µm Hg) and at T=353 K for 3 hours. For the measurement of the samples, a program was used that collects about 100 data points (50 each for adsorption and desorption) evenly distributed between P/P_0=0.02 and P/P_0=1. For some graphite samples only BET models could be fitted to the data.

2.2.5 Determination of the pH

A mass of 0.05g of activated carbon was mixed in 50 ml of distilled water at a temperature of 25ºC to determine the pH of the solution containing the activated carbon. After agitation, the pH of each sample was measured.

3. RESULTS AND DISCUSSION

3.1 Influence of Preparation Parameters

Five activated carbon samples labelled M10-24-100, M10-60-100, MAPZC3, MAPZC4, and MAPZC5 were obtained. The parameters varied in the preparation of the activated carbon samples (yields, impregnation ratio (IR) and CR chemical recovery for each sample) are presented in Fig. 3. This Fig. shows the parameters that determine the influence of the activating agent $ZnCl_2$, its physical status and on the basis of activation in the procedure processing of the activated carbon. It also makes it possible to investigate the part of the cobs which would give the best activated carbon taking into account the fact that the maize cob has rather a complex natural structure (a hard part and a light part). Cagnon et al. (2009) showed that the calculated yields do not take into account the amount of raw material used and that the weight contribution of the hemicelluloses ranges between 14.1% and 24.5%, the cellulose from 5.6% and 27.6% and the lignin from 55.0% to 79.0%. These authors concluded that lignin can be considered as being the major weight contributor to all chars and the cellulose and hemicellulose weight contribution not negligible. Thus the works of Cagnon et al. (2009) explain why the materials M10-60-100 and M10-24-100 prepared from the soft part of the cobs (consisting mainly of cellulose and hemicelluloses) (Maha et al. (2010)) have low yields compared to the other materials. Furthermore the carbon MAPZC5 produced from hard part of cob, which contained a great amount of lignin gives a yield of about 35.63% far greater than the yield of samples M10-60-100, M10-24-100 and MAPZC3. The yield of the sample MAPZC4 42.91% is explained by the high content of zinc chloride $ZnCl_2$ (3g) used in the preparation of this material even though the raw material used in its preparation.

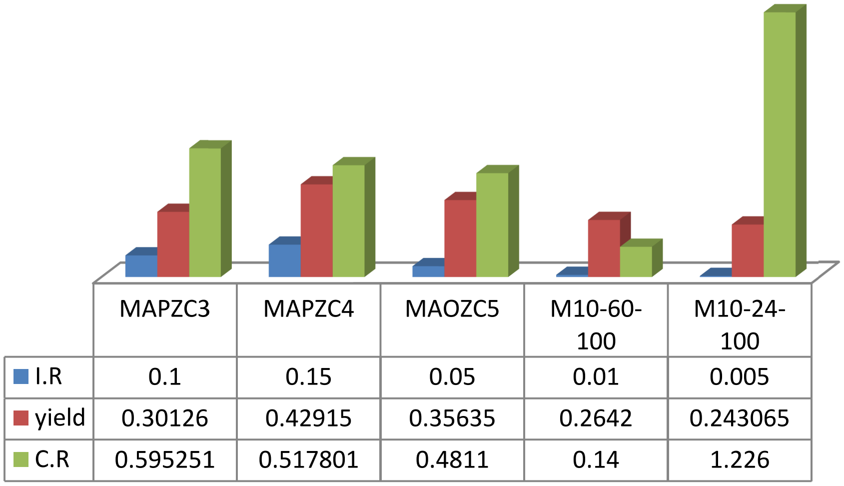
During the preparation of the activated carbon of maize cobs, several parameters were varied (Table 1)—particles size of the particles, concentration or mass of the activating agent, physical state of the activating agent (solid or liquid), time of residence, part of the cobs used (light part or girdles woody).With practically the same experimental conditions, several authors such as Aber et al. (2009) (activation with K_2HPO_4 at 700ºC), Boudrahem et al. (2009) (activation with $ZnCl_2$ at 600ºC with a rate of 10ºC/min), Adinata et al. (2007) (activation with K_2CO_3 at 600-800ºC with a rate of 10ºC/min), Kumar et al. (2010) (activation with 24% NaOH at 165ºC), Qiang et al. (2007) (activation with $ZnCl_2$ at 400-900ºC) and Koutcheiko et al. (2007) (activation with NaOH at 600ºC with a rate of 5ºC/min) obtained activated carbon with very good characteristics with activated carbon sample having specific surfaces reaching 2170 m^2/g and porous volumes being able to reach 1.70 cm^3/g in the case of the work of Qiang et al. (2007) for example.

Taking into account previous works referred to the above preparation of activated carbon starting from vegetable precursors, parameters such as the maximum temperature, heating rate, the temperature of cooling, were maintained at constant values in this work. The impregnation ratios retained in this work are those having provided better results in the literature (Avom, 1982; Avom et al., 2001; Ibañez, 2002; Nono, 1989). Indeed, according to

Tsai et al. (1998), the most important parameter in chemical activation of maize cobs with zinc chloride ($ZnCl_2$) was found to be impregnation ratio (IR), this is why a particular accent was related to this parameter. The other parameters are rather traditional and practically standard in the majority of works with maize cobs (Chang et al., 2000; Tsai et al., 1998; Tsai et al., 2001). In addition, the cobs with soft structure do not require high carbonization temperature values (compared to the temperatures generally used in the preparation of the activated carbon by physical activation for example), thus, 500ºC is a satisfactory temperature for this process. As for heating rate, 10ºC/min is considered slow. At this rate, very few volatile compounds are observed to be present in final material and the original structure of material is generally preserved (Ibañez, 2002; Soltes and Elder, 1981). The use of zinc chloride $ZnCl_2$ as activating agent prevents the formation of tars which blocks the pores (Avom, 1982). Chemical activation by $ZnCl_2$ improves the pore development in the carbon structure, and because of the chemical effects, the yields of the obtained activated carbon are usually high (Ahmadpour and Do, 1997) (Fig. 3). The decomposition gases were maintained in the apparatus because they make it possible to obtain activated carbon with better adsorbent properties than those obtained in vacuum (or in inert atmosphere) or with other gases such as O_2, CO_2, N_2 (Avom, 1982).

As observed previously, intense vapours appeared during the preparation of the various activated carbon samples between 200ºC and 400ºC. These vapours are stabilized around 400ºC and then stop completely at this temperature except for the MAPZC5 sample where the vapours stop only after having reached the maximum temperature of 500ºC. It is the decomposition of the various components of vegetal cells combined with the simultaneous activation of zinc chloride which are in all the cases at the origin of these intense vapours (Avom, 1982; Soltes and Elder, 1981). Indeed between 150ºC and 300ºC, the cellulose loses its structural water (Avom, 1982) between 200ºC and 260ºC occurred the decomposition of hemicelluloses, and that of cellulose between 240ºC and 350ºC. During these two decompositions, rupture of the C-O and C-C bonds occurs, as well as the rupture of the chains or depolymerisation (Tang and Bacon, 1964). The degradation of lignin is observed from 280ºC and is completed only after 500ºC. This explains why in the MAPZC5 sample, which consists primarily of the woody belt (hard part of the cob), intense vapours are observed even after having reached the maximum temperature because this precursor would contain more lignin than all the others in which the vapours practically stop in the vicinity of 400ºC. The samples containing less zinc chloride $ZnCl_2$ produce more vapours than the others.

Fig. 3 represents the impregnation ratios (I.R), the chemical recovery C.R and the yields of the activated carbon of maize cobs. Generally, this data reveals that the I.R strongly influences the yield. Indeed, the higher the impregnation ratio, the higher the yield of the final material. Except for the M10-60-100 sample, the CR for all the samples is higher than the yield. The time of residence also influences the yield of the final material; the higher the activated carbon is maintained at the maximum temperature, the lower the yield (sample M10-60-100 and M10-24-100).



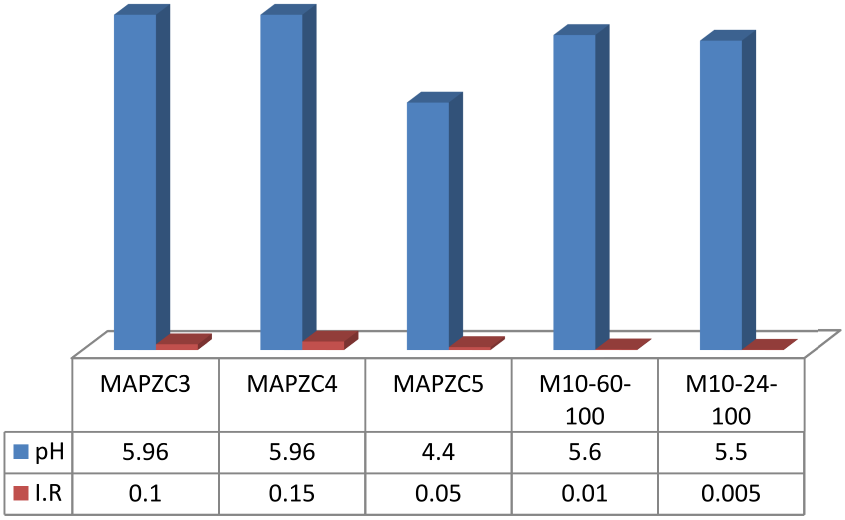
	MAPZC3	MAPZC4	MAOZC5	M10-60-100	M10-24-100
🟦 I.R	0.1	0.15	0.05	0.01	0.005
🟥 yield	0.30126	0.42915	0.35635	0.2642	0.243065
🟩 C.R	0.595251	0.517801	0.4811	0.14	1.226

Fig. 3. I.R, yields and C.R of the activated carbon of maize cobs

Yield is obtained from the values of Table 1 by using equation yield (%) =mass of obtained activated carbon/initial mass of maize cobs×100; IR is obtained from the values of Table 1 by using the equation IR=mass of $ZnCl_2$/initial mass of maize cobs; CR is obtained from the data of Table using the formula CR= (mass of carbon before washing-mass of carbon after washing)/mass of impregnated $ZnCl_2$

3.2 pH of the Activated Carbon of Maize Cobs

The pHs of all the studied activated carbons are found on Fig. 4. This Fig. also represents the values of pH of the various prepared activated carbon samples according to the impregnation ratio I.R. It is observed that the impregnation ratio influences these pH values. All the pH values were found to lie between 2 and 12.5 thus the activated carbon of maize cobs cannot be considered priority as hazardous wastes matters and are not corrosive (University of Monreal-Quebec, 2008). It is noted that for all materials, the pH's are not very acid as they are higher than 5, except for the MAPZC5 sample which has a pH lower than 5. This could be explained once again by the part of the cob used for the preparation of this sample. As explained previously, the woody part (hard part of the cob) was used, exclusively, for the preparation of this material. This part of the maize cob is predominantly made up of lignin (Igwe and Abia, 2003; Suresh and Jackson, 1971; Tuah and Orskov, 2010) and the carbonization of lignin produces very small quantity of ash (Ibañez, 2002; Nono, 1989; Suresh and Jackson, 1971). This weak ash content explains the high yield of this sample (Fig. 3) and for this reason the pH of this material is more acid than that of the others. Indeed, the activated carbon resulting from the precursors having low ash contents have weak pH (Montanher et al., 2005; Suziki et al., 2007). In addition, the four samples whose precursors and particles thickness are identical (M 10-60-100, M10-24-100, MAPZC3, MAPZC4), it's observed on Fig. 4 that the higher the pH, the more the I.R is large, thus the quantity of $ZnCl_2$ used for the activation of the cobs influences slightly the pH of the activated carbon. Commercial sample OA00 has a basic pH of 9.34 contrary to the pH of the activated carbon of maize cobs (Fig. 4). This value of pH is due to the rather high ash content of this sample. This ash content is explained by the presence of minerals in material OA00 (see XRD spectrum result), particularly silica (Zawadzki, 1989).



	MAPZC3	MAPZC4	MAPZC5	M10-60-100	M10-24-100
🟦 pH	5.96	5.96	4.4	5.6	5.5
🟥 I.R	0.1	0.15	0.05	0.01	0.005

Fig. 4. I.R and pH of the activated carbon of maize cobs

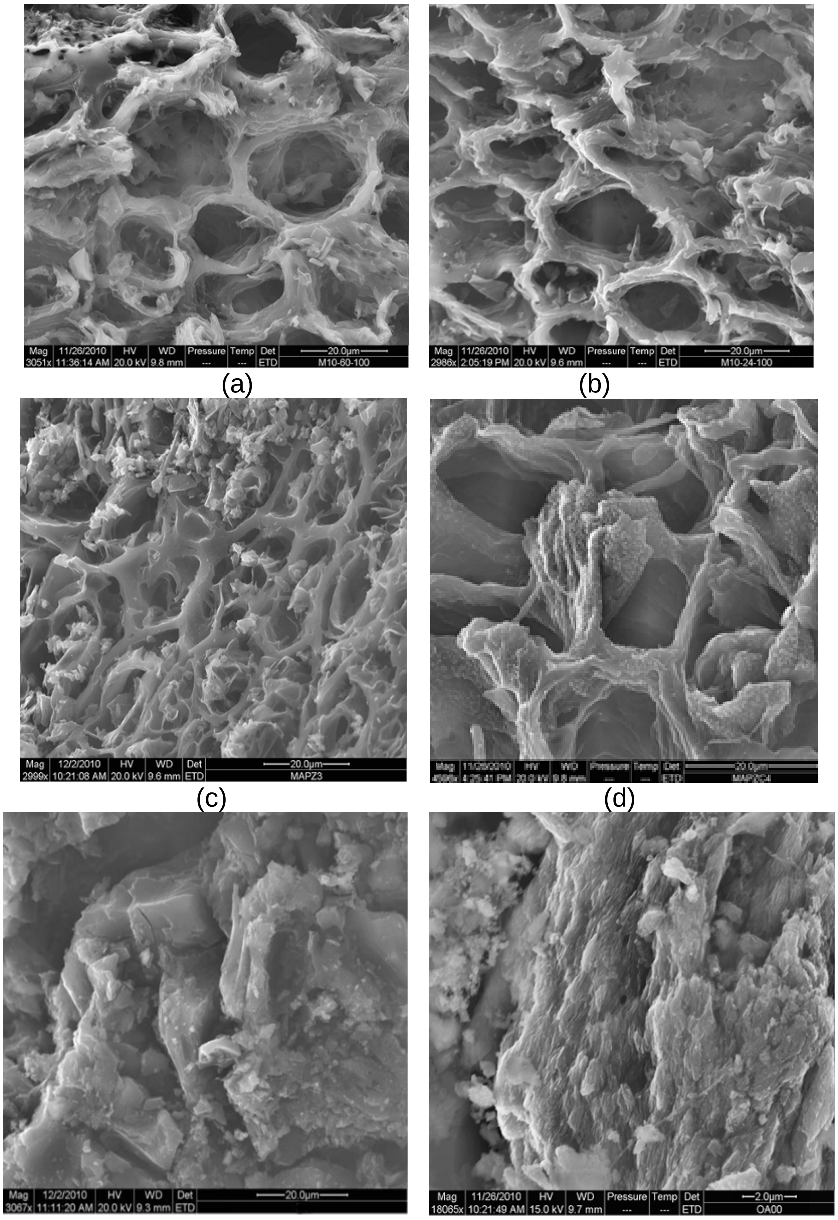
pH of solution containing each maize cobs activated carbon; IR is obtained from the values of Table 1 by using the equation IR=mass of $ZnCl_2$/initial mass of maize cobs

Several authors in the past limited their characterization of activated carbon to traditional techniques such as determination of iodine numbers (Aygün et al., 1989), X-ray fluorescence (Bhagavathy et al., 1991), the determination of specific surface area by B.E.T only (Khalili et al., 2000). This work has the advantage of employing a diverse number of state of the art techniques of characterization which provide results with much greater precision.

The methods of characterization particularly simultaneous SEM-EDX analysis are a major innovation. In fact in the literature (Malarvizhi and Sulochana, 2008; Prahas et al., 2008), these analyses are usually made separately and EDX analysis in this work which gives qualitative and quantitative chemical composition takes into account the heterogeneity of the surfaces what is not taken into account by EDX analysis traditional met in the literature insofar as in the majority of work it is the x-ray fluorescence which was generally used (Abiko, 2011). Thus in this work, these analyses are much more precise. In addition the study of porosity is also an innovation because in the majority of work (Prahas et al., 2008) this analysis gives only quantities adsorbed according to the partial pressures and specific surfaces and the other parameters of porosities such as porous volumes, the size of the particles are given in an indirect way. In this work, all the results (specific surfaces (B.E.T, B.J.H, and single point), porous volume, and sizes of the particles) are directly given.

3.3 SEM-EDX Analysis-Samples' Surface and Chemical Compositions

SEM micrographs of surfaces of the studied activated carbon represented by Fig. 5 shows that the activated carbon of maize cobs presents all of the cavities to the level of their surfaces. Samples M10-60-100, M10-24-100, MAPZC3 and MAPZC4 show surface heterogeneity and have very varied structures.



(a) (b)

(c) (d)

(e) (f)

Fig. 5. Images of the activated carbons by SEM

(a) carbon M10-60-100 (Magnitude: 3051x ; HD: 20.0kV; W.D: 9.8mm; Size: 20.0µm); (b) carbon M10-24-100 (Magnitude: 2986x ; HD: 20.0kV; W.D: 9.6mm; Size: 20.0µm); (c) carbon MAPZC3 (Magnitude: 2999x ; HD: 20.0kV; W.D:9.6mm; Size: 20.0µm); (d) carbon MAPZC4 (Magnitude: 2999x ; HD: 20.0kV; W.D: 9.8mm; Size: 20.0µm); (e) carbon MAPZC5 (Magnitude: 3067x ; HD: 20.0kV; W.D: 9.3mm; Size: 20.0µm); (f) carbon OA00 (Magnitude: 18085x ; HD: 15.0kV; W.D: 9.7mm; Size: 2.0µm)

All these material are porous in appearance. Sample MAPZC4 presents pores which are, apparently, more open (broad) compared to MAPZC3 material, which is explained by difference in mass of the activating agent used in these materials (3g for MAPZC4 and 2g for MAPZC3) (Table 1). Indeed, the zinc chloride $ZnCl_2$ permits the development of the porosity of materials, so the more there is in the precursor, the more the pores of the activated carbon are opened (Ahmadpour and Do, 1997). The activated carbon MAPZC5 has a compact structure and its surface is different from the first samples although the precursor is the same for all these chars. However, it is the hard part of the cob which was used for the latter sample which is what certainly explains this difference in surface structure. In addition, MAPZC5 has a homogeneous structure with a more developed porosity when compared to the other similar samples because in this material some micropores are observed. The commercial sample of animal origin labelled OA00 is similar to the MAPZC5 sample with a compact and homogeneous surface on which a few micropores are observed.

For the activated carbon having heterogeneous surfaces, analysis EDX was carried out on several zones of material. The results of analysis EDX of studied coals (Table 2) show that these materials primarily consist of carbon and oxygen to very varied proportions. It's important to note the presence of the rather high Zn contents in materials MAPZC4, MAPZC3, M10-60-100 and M10-24-100 coming from the activating agent $ZnCl_2$. The MAPZC4 sample, particularly, shows zinc contents going up to 57% per region on its surface what could considerably reduce the adsorbent properties of this material. This excess zinc could, for example, block certain active sites and prevent the adsorption of some compounds and metals. EDX analysis of the sample MAPZC5 practically does not show the presence of Zinc; neither does it show chlorine which could explain the rather good adsorbent properties observed particularly for this activated carbon (Dina et al., 2012).

Table 2. Qualitative and quantitative analysis (into % massic) of the activated carbon by EDX

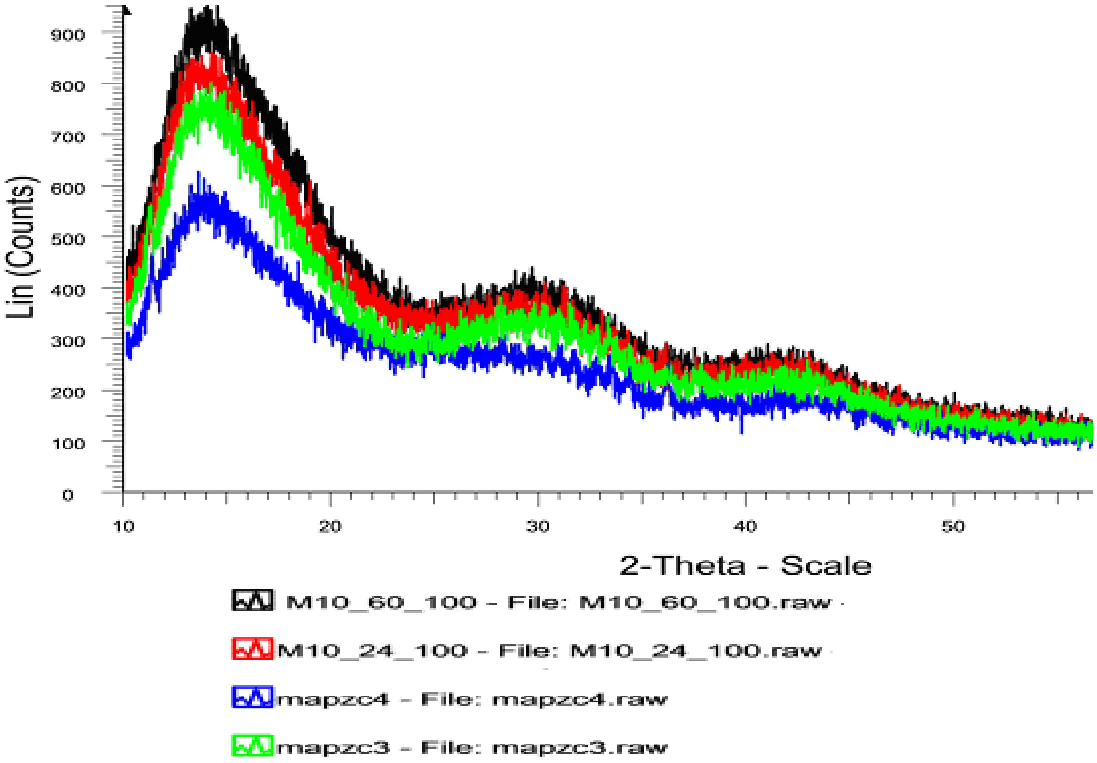
Sample	**C**			**O**			**Si**		
	[f]max	**[g]min**	**[h]mea**	**max**	**min**	**mea**	**max**	**min**	**mea**
M10-60-100	90	60	80	18	3	7	14	0	2
M10-24-100	90	70	80	16	2	9	3	0	1
MAPZC3	90	80	80	21	4	10	1	0	0
MAPZC4	80	40	60	10	2	6	1	1	1
MAPZC5	90	70	80	27	6	16	4	0	1
OA00	30	10	10	57	31	40	-	-	-
Sample	**Ca**			**Zn**			**P**		
	Max	min	mea	max	min	mea	max	min	mea
M10-60-100	2	0	0	17	0	2	-	-	-
M10-24-100	-	-	-	13	1	3	-	-	-
MAPZC3	-	-	-	10	0	2	1	0	0
MAPZC4	-	-	-	57	4	25	-	-	-
MAPZC5	-	-	-	-	-	-	-	-	-
OA00	70	19	29	-	-	-	30	10	15

[f]max=maximum; [g]min=minimum; [h]mea=mean

3.4 X-rays Studies

For each activated carbon sample, XRD analysis was carried out several times. XRD patterns of the activated carbon of maize cobs are represented on Figs. 6a-6b). These reveal that all these coals are amorphous. The amorphism observed is explained by the rupture of multiple bonds C-C (mainly those of the aromatic rings) and the formations of the groups and functions on the surface (see result FTIR on Fig. 7) during the preparation. In addition, the observation of these spectra makes it possible to explain the characteristic of the material MAPZC5. Just like samples M10-60-100, M10-24-100, MAPZC3 and MAPZC4, the MAPZC5 material is amorphous but has other humps on the base line than the previous four (Fig. 6b). This characteristic could be explained not only by the precursor being predominantly made up of the woody belt, as explained previously, but also by the elementary chemical composition of this sample (EDX results, Table 2). Indeed, the proportions of cellulose, hemicellulose and lignin are different in the two parts of the maize cob. Taking into account the phenomena observed during the preparation of this activated carbon (gases and liquid released), it appears that the soft part of the cob contains mainly cellulose and hemicellulose, both having linear polymeric structures of residues of glucose (Igwe and Abia, 2003; Nangole et al., 1983). The hard part also contains lignin with rigid covalent bonds between various phenolic groups; that's why the elementary chemical composition of the sample MAPZC5 (EDX result on Table 2) is different from that of the other maize cobs activated carbon with a diversity of elements compared to the other samples. This characteristic could also produce particular properties (specific surface area, porous volume, surface function, and textural structure and EDX results) of this sample compared to the others.

(a)



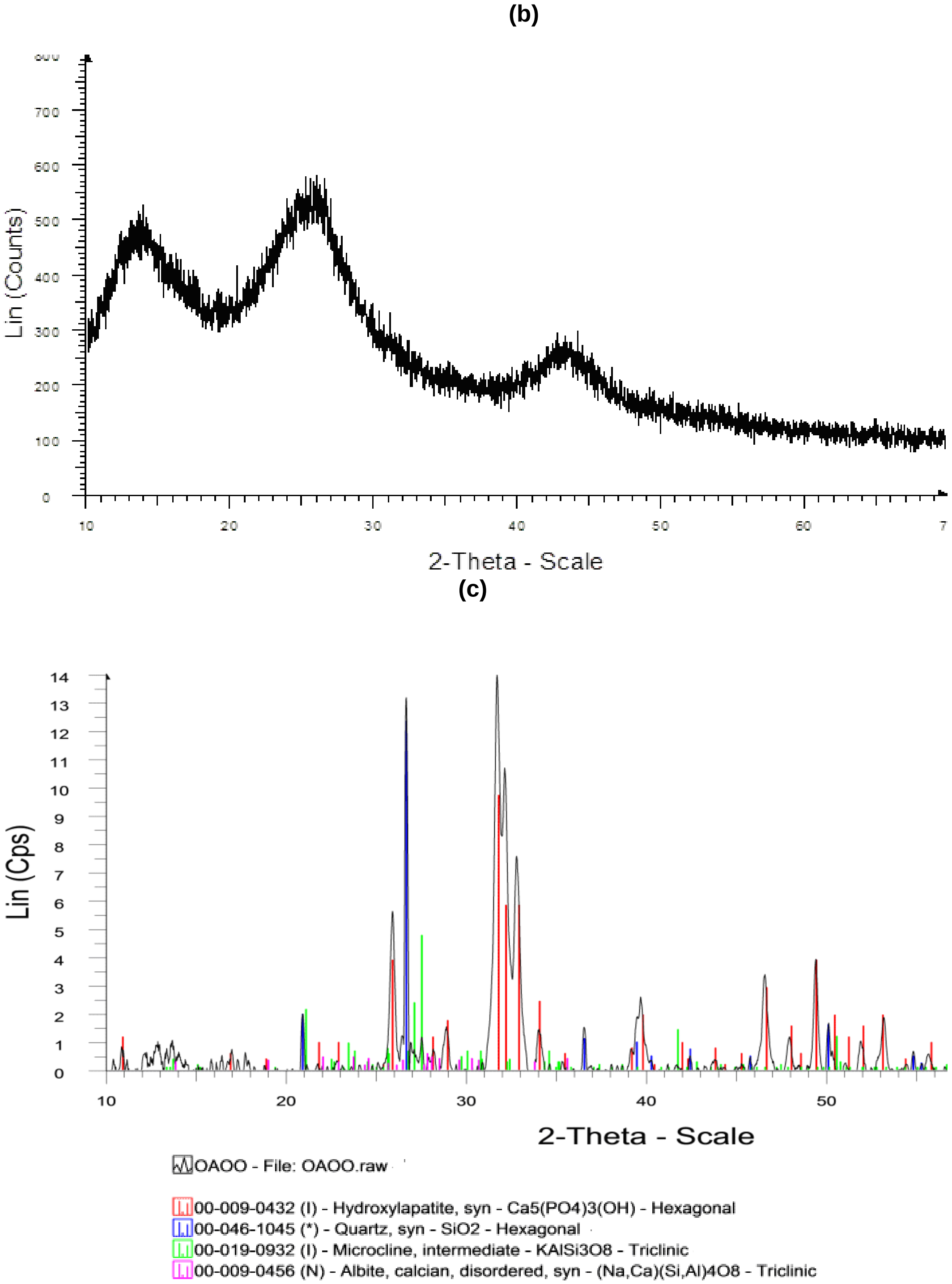


Fig. 6. XRD patterns of the studied activated carbon

(a) Samples M10-60-100, M10-24-100, MAPZC3, MAPZC4 obtained from the light part of the cobs (b) Sample MAPZC5 obtained from the hard part (c) commercial activated carbon sample OA00

Tangjuank et al. (2009) obtained practically identical XRD spectra with activated carbon obtained from cashew nuts shells by physico-chemical activation (KOH/CO_2). These results confirm the fact that the activated carbon obtained from agricultural wastes are for the majority of times amorphous because of the existence of probable surface functions from which the crystallization is difficult.

X-ray pattern of the commercial sample, OA00, (Fig. 6c) unlike the activated carbon of maize cobs, represent a material which crystallizes. The examination of this spectrum highlights the presence of minerals such as hydroxyapatite, quartz, feldspar traces (microcline and white feldspar). The presence of these minerals could explain the adsorbent properties of this material particularly hydroxyapatite (Amer et al., 2010; Liao et al., 2010; Mobasherpour et al., 2011).

3.5 FTIR Analysis-Functional Groups Study

The surface of the activated carbon generally consists of functional groups which are oxygenated sites and possibly of the amino sites (Ibañez, 2002; Shen, 2008). The IR absorption spectra in solid phase recorded of the activated carbon of maize cobs and of commercial sample OA00 are presented in Fig. 7.

At low temperature range of carbonization of the activated carbon, some functional groups are observed on the surface of these coals. For all the maize cobs activated carbons, FTIR spectra (Figs. 7a-7b) showed that there are two bands characteristic of aliphatic groups -CH_3 and - CH_2- around 2846 cm^{-1} and 2950 cm^{-1} (Tang and Bacon, 1964; Vinke el al., 1994). Around 3200-3500 cm^{-1} vibration of OH appears in all the samples, suggesting the presence of the hydroxyls groups and chemically absorbed water on the surface. The presence of the peaks around 1600 and 1620 cm^{-1} suggests the presence of carbonyls C=O groups coming from the stretching of the C=C bond (Akhter et al., 1985; Tuah and Orskov, 2010). Indeed under the effect of heat, there is rupture of C=C bonds and the presence of OH bonds leads to the formation of C=C groups. Most researchers like Ibañez (2002) (prepared the activated carbon by chemical activation with sulphuric acid H_2SO_4 on the olive cores and apple pulps) and Bikales and Segal (1971) (studied the carbonization of cellulose and cellulose derivatives) have estimated that one of the intermediate products leading to the passage of the C=C bond to C=O is levoglucosan whose formation takes place between 200 and 400ºC (Vinke et al., 1994). The association of OH bonds and C=O predicts the existence of carboxylic acid groups–COOH which further explains the acidity of the activated carbon of maize cobs. The peaks observed around 1290 cm^{-1} are characteristic of ν (CO) vibrations coming from the ether or aliphatic groups (Ibañez, 2002; Serrano et al., 1999). The vibration of deformation ν (CH_2) is observed around 1420 cm^{-1} (Ibañez, 2002; Zawadzki, 1989). The lines observed around 1450-1500 cm^{-1} could correspond to the vibrations in the plan of the aromatic rings (Khalil, 1999). The samples M10-60-100, M10-24-100, MAPZC3 and MAPZC4 present all of the lines around 1050 cm^{-1} and 1100 cm^{-1} characteristic respectively of primary and secondary alcohols (Fig. 7a). The series of lines between 700 and 800 cm^{-1} is characteristic of the vibration ν (CH) correspondent with systems with 1,2,3,4 or 5 adjacent hydrogen atoms (Brand and Eglinton, 1945) (Figs. 7a and 7b). Tangjuank et al. (2009) in the same work mentioned above obtained similar IR spectra and obtained the same functional groups.

The spectra of the samples M10-60-100 and M10-24-100 are practically identical and thus present the same groups on the surface, as deduced from the similar method of preparation and the precursor. However, the overlapping of lines observed between 1809 and 1034 cm^{-1}

in the spectrum of the M10-60-100 material is less marked in the M10-24-100 sample; an observation which leads us to predict a reduced number of functional groups in this sample. The relatively long residence time (24 hours at 500ºC) of the M10-24-100 sample characterized by the reduction of surface functions, could explain this difference (Darnell et al., 1990).

Samples MAPZC3 and MAPZC4 have similar spectra for the same reasons as previously explained but in this case MAPZC3 seems to have a greater number of groups. This could be explained by its impregnation ratio (I.R) which is lower than that of MAPZC4 (Fig. 3). Indeed, the zinc excess observed by EDX in char MAPZC4 would certainly have prevented the formation of certain groups (oxides for example) in great number. In addition the band around 3500 cm^{-1} of sample MAPZC3 is lower than that of MAPZC4 what marks the presence of the relatively strong hydrogen bridges in MAPZC3 (Biniak et al., 1997).

Fig. 7b show peaks characteristic of aliphatic esters, of the groups C=O and C-O which are accentuated and more visible in this sample (MAPZC5) obtained from the woody belt (hard part of the cob). This may further explain why the pH of this material is most acid (pH=4.4).

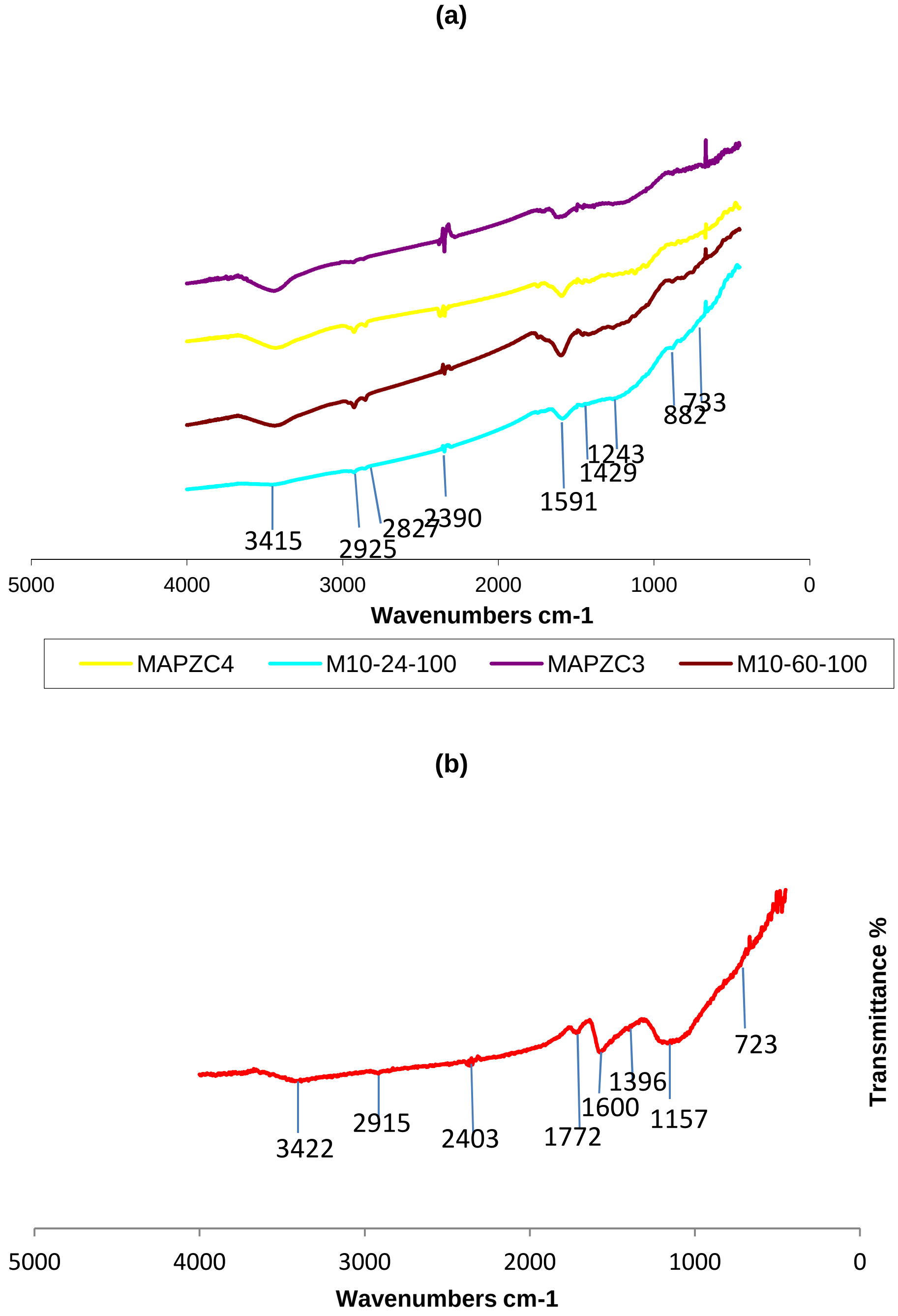
FTIR spectrum of the commercial sample OA00 is completely different from that of the activated carbon of maize cobs (Fig. 7c). This spectrum presents nevertheless, certain groups present in the maize cobs activated carbons such as OH characterized by the band of vibration at 3446 cm^{-1}, aliphatic groups - CH_3 and - CH_2- around 2880 and 2950 cm^{-1}, and the vibrations ν (CH) between 700-800 cm^{-1}. The presence of a very significant number of groups CO (very intense peak at 1034 cm^{-1}) is observed. At 1664 cm^{-1} a bending characteristic of the NH is observed which explains the basicity of this material. Three bands characteristic of groups C=C (1498, 1457 and 1416 cm^{-1}) being certainly in aromatic rings are also observed.

There exists coherence between the values of pH of various materials (Fig. 3) and the identified functional groups. The acid groups found on the activated carbon of maize cobs explain explicitly, why the pH's of these chars are all acid.

3.6 Brunauer-Emmett-Teller (BET) Surface Area and Porosity Studies

The specific surfaces area determined by BET, the total pore volume obtained by adsorption at a given point (definite relative pressure) and for a given pore size are summarized in Table 3. The pore size obtained by BET using the relation 4V/A of activated carbon of maize cobs and commercial sample OA00 are also shown in Table 3.

Specific surfaces area of the chars obtained from the soft part of the cobs (periphery and marrow) associated with negligible particles of woody belt are very weak and especially very difficult to determine because of the volatility of these materials. These values vary between 0.43 m^2/g for the M10-60-100 sample and 11.62 m^2/g for the sample MAPZC4 (Table 3). These low values of specific surfaces show that the entry of the gas molecules N_2 in the existing pores is very restricted and even impossible for these samples such as M10-60-100. In addition, the comparison of specific surface area of the samples M10-60-100 (0.43 m^2/g) and of the sample M10-24-100 (5.26 m^2/g) makes it possible to explain the influence of the time of residence on the preparation of the activated carbon of maize cobs. Indeed, the longer the residence time, the higher the specific surface area and the more the pores are opened (0.000279 cm^3/g for M10-60-100 with residence time of 1 hour and 0.002713 cm^3/g for M10-24-100 with a residence time of 24 hours).


(a)
3415
2925
2827
2390
1591
1429
1243
882
733
5000
4000
3000
2000
1000
0
Wavenumbers cm-1
MAPZC4
M10-24-100
MAPZC3
M10-60-100
(b)
Transmittance %
3422
2915
2403
1772
1600
1396
1157
723
5000
4000
3000
2000
1000
0
Wavenumbers cm-1

(c)

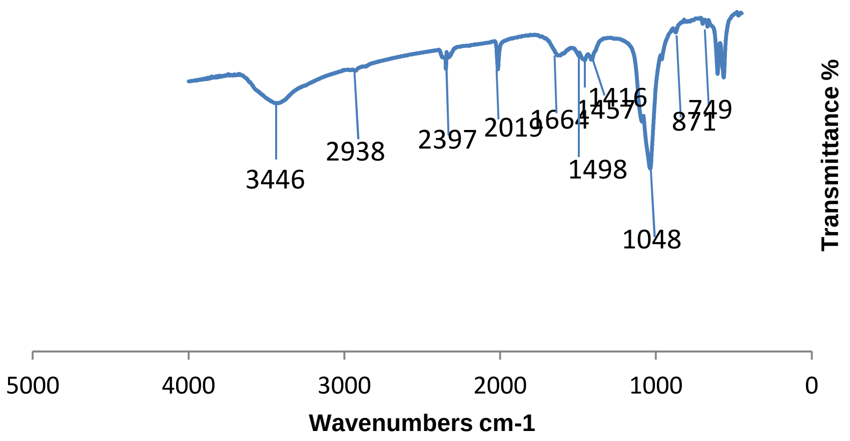


Fig. 7. FTIR spectra of the activated carbon of the maize cobs
(a) M10-60-100, M10-24-100, MAPZC3, MAPZC4, (b) MAPZC5 and (c) sample OA00

The impregnation ratio (IR) also affects the specific surface area and porosity. The higher the IR, the higher the specific surface area and porous volume for materials produced from the same precursor. Thus, samples MAPZC3 with impregnation ratios of 0.1 has a specific surface area of 7.13 m^2/g and pore volume of 0.0022 cm^3/g while MAPZC4 with an impregnation ratio of 0.15 has a specific surface area of 11.62 m^2/g and a porous volume of 0.11 cm^3/g. Consistent with the described trend, the specific surfaces area of MAPZC3 and MAPZC4 are by far higher than those of the M10-60-100 and M10-24-100 with 0.005 as impregnation ratio (IR).

It is interesting to note that the MAPZC5 sample obtained from the woody belt has a higher specific surface of about 701.68 m^2/g and a porous volume of 0.39 cm^3/g; values by far higher than those given with the chars obtained with the light part of the cob. Tangjuank et al. (2009) quoted above obtained similar results with agricultural wastes (cashew nut shells) activated carbon with a maximum specific surface area by B.E.T of about 627 m^2/g while Qiang et al. (2007), with the same activating agent as in this work, obtained a high value of specific surface area of about 2170 m^2/g and porous volume of about 1.70 cm^3/g. These high values could be explained may be by the raw materials used by Qiang et al. (2007) (cattle-manure compost) or by the temperatures used which attained 900ºC. Some differences in preparation techniques like the treatment of the raw material and the impregnation ratio (I.R) could also explained these high values.

The BET specific surface area and porous volume values of sample MAPZC5 are significant than those of the commercial sample OA00 (81.09 m^2/g and 0.18 cm^3/g for specific surface and porous volume, respectively).

Table 3. Specific surfaces area and porosities of the activated carbon of maize cobs and of commercial sample OA00

Adsorbent	[I]B.E.T specific surface area (m^2/g)	[J]Pores volumes (cm^3/g)	Pores sizes (Å)
M10-60-100	0.4312	0.00028	25.8580
M10-24-100	5.2605	0.00271	20.6325
MAPZC3	7.1314	0.00220	12.3190
MAPZC4	11.6202	0.10817	72.3636
MAPZC5	701.6853	0.3938	22.4505
OA00	81.8638	0.1766	85.2648

[I]BET specific surface area: Brunau-Emmett-Teller specific surface area obtained using BET linear transformer equation from the data of Fig. 7; [J]porous volume obtained using BET equation

4. CONCLUSION

The activated carbons from agricultural wastes, maize cobs, were obtained under different operating conditions and characterized. The structural properties of samples obtained from the soft part and some particles of woody belt are not significant (very weak specific surfaces varying in the interval 0.43 m^2/g-11.62 m^2/g and porous volumes between 0.0002 cm^3/g and 0.11 cm^3/g and absence of microporosity). But some acidic functional groups are observed at the surface of these materials. On the other hand, MAPZC5 obtained from the woody belt showed higher values of physico-chemical properties; a specific surface area of about 701.68 m^2/g and a porous volume of approximatively 0.39 cm^3/g. These values are higher than those of the commercial sample of which the specific surface area and the porous volume are respectively equal to 81.09 m^2/g and 0.18 cm^3/g). SEM micrograph of the MAPZC5 material reveals a structure completely different from the four other samples resulting from the same precursor with appearance of some micropores what explains the great difference at the level of the values in specific surface area and volume porous.

On the surface of all the activated carbons produced from maize cobs, some acidic functional groups are observed. It is shown that the long residence time considerably decreased the number of functional groups on the surface of these chars as well as the $ZnCl_2$ content in the precursor. Some micropores and basic functional groups are observed on the surface of the commercial activated carbon OA00. This material is the only one which crystallized and some minerals such as quartz and hydroxyapatite mainly responsible for the strong adsorption capacity are observed. In addition, the values of pH showed that these activated carbons are neither dangerous nor corrosive; that is why they can be used in the purification of water, waste water and in agribusiness industries. The experimental results indicated that this method of preparation of chars is easy, economic and activated carbon obtained particularly from the hard part of the cob has very significant physico-chemical and structural properties. Agricultural wastes, particularly maize cobs can be an alternative. These activated carbons can mainly be used in the purification of the consumption of water in Cameroon where water sources are abundant but requires treatment.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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