PHOSPHORIC ACID-ACTIVATED CARBONS DEVELOPED FROM MAIZE STALKS AND THEIR APPLICATIONS TO HEAVY METAL REMOVAL

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ABSTRACT

Activated carbons (ACs) were prepared by pyrolysis of maize stalks (MS) in presence of phosphoric acid. MS were impregnated with aqueous solutions of H_3PO_4 following the variant impregnation method. Three concentrations were used to produce impregnation ratios of 50, 75 and 100 wt%. The activation process was carried out at 773 K in a current of N_2 flow. The acid-carbon samples were designated MP25, MP50 and MP75, respectively. The char MC500, and the single-step steam pyrolysis MS700, samples, were also prepared. The porous structure of the five carbons was investigated by N_2 adsorption isotherms at 77K and analyzing the data using BET equation as well as both α_s and t methods. A characteristic feature of the prepared carbons indicates that considerable fractions of the surfaces are located in non-microporous area. The mechanisms of H_3PO_4 and single-step steam activations of MS for the evolution porosity were proposed. A thermogravimetric study showed that H_3PO_4 was capable to suppress the evolution of tarry substances during carbonization and thus increases both carbon yield and carbon-thermal stability. The microcrystallinities and surface properties of the carbons prepared were characterized using an X-ray diffraction analyzer, scanning electron microscope SEM, as well as the Fourier transform infrared FTIR. The equilibrium adsorption capacities of the investigated samples towards Pb^{2+} uptake were determined with the Langmuir and Freundlich equations and found to be between 57 and 358 mg/g. The suggested mechanism in Pb^{2+} uptake from aqueous solutions was based not only on carbon pore-structure but also on the ion exchange capacity together with the carbon surface-pH.

Keywords : Maize stalks; acid-activated carbon; Pb^{2+} removal.

1. INTRODUCTION

Activated carbons are extremely versatile adsorbents of major industrial significance and are used in a wide range of applications which are concerned principally with the removal of organic and inorganic species by adsorption from the liquid or gas phase [Toles et al. (1998); El-Hendawy (2005); Youssef et al. (1992); Youssef et al. (2004); El-Hendawy (2003) and Sato et al., (2007)]. Although activated carbon can be made from a variety of raw materials yet, practically, ACs are still produced from a limited number of precursors on the worldwide level, i.e.coal. wood and coconut shells. These precursors are not available in many countries and their importation will raise the cost of the end product. Thus it becomes necessary to develop ACs from locally available feedstocks. Agricultural by-products and wastes present highly recommended feedstocks. There are many studies in the literature related to preparation of activated carbons from agricultural wastes [Jagtoyen & Derbyshire (1998); Guo & Rockstraw (2007); El-Hendawy (2001); Laine et al. (1989); Molina-Sabio et al. (1995) and Gerogova et al. (1996)]. However, there is only few research on preparation of activated carbons using maize stalks [Youssef et al. (2004)]. In this study, the proposed research program is directed to prepare ACs from MS facing two problems at the same time: minimizing pollution by getting rid of this agricultural waste and developing a low cost adsorbent for the removal of pollutants.

Activation with phosphoric acid is one of the best technologies to manufacture acidic-ACs [Toles et al. (1998); Jagtoyen & Derbyshire (1998); Guo & Rockstraw (2007); El-Hendawy et al. (2001); Laine et al. (1989) and Molina-Sabio(1995)]. It realizes many recommending aspects: (i) it is a single-step with respect to heat treatment (ii) it is conducted at low temperature 673-773K saving thus energy consumption (iii) it restricts gaseous evolution and thus enhances carbon yield (35-50%). besides (iv) a wide variety of activated carbons are possible to be obtained upon varying acid concentrations. Thus, good adsorbent carbons are obtained with no contaminants, as the case with the previous $ZnCl_2$ processes which consider itself as a contaminant if the traces of it rest in carbons. Recently, a single-step steam pyrolysis was proposed and applied by many authors [Gerogova et al. (1996); Warhurrst et al. (1997) and El-Hendawy (2005)]. It accepts a premium importance for

production of good ACs and by saving energy as well besides it is conducted without any chemical.

It is worthmentioning that pollution, nowadays, becomes one of the most urgent problems which threat the environment and public health. Application of AC adsorption systems has emerged and been identified as one of the most effective technologies for the removal of impurities from air, gas and liquid mixtures eventhough the contaminants are present only in trace amounts (ppm). Lead is one of the most toxic heavy metals among the potentially toxic heavy metal list. Lead poisoning in human causes severe damage to the kidney, nervous system, liver and brain. For these reasons lead was chosen as the study heavy metal. In this study two new types of activated carbons are explored with respect to the lead removal from aqueous solutions. One is phosphoric acid-activated carbon and another is steam activated carbon derived from maize stalks.

The objective of the present work was to study the possibility of preparing effective activated carbons from maize stalks by different activation schemes, determining their textural and surface chemical properties and to determine their efficiency in the removal of Pb^{2+} from aqueous solutions. Various techniques were used such as N_2 gas adsorption, FTIR, SEM, XRD, in addition to TG.

2. EXPERIMENTAL

2.1 MATERIALS

Maize stalks were washed and then pre-dried at $80^{\circ}C$ for 48h. The dried product was milled and sieved. The fraction of particle size 1-3 mm was washed with 5 % N HCl, tap water and finally with distilled water and then drying at $80^{\circ}C$ for overnight. Impregnation with 50,75 and 100% by weight phosphoric acid (Analar) was continued for 24h before drying at $100^{\circ}C$ overnight. The resulting massed were then carbonized in a tubular furnace, in nitrogen atmosphere at $500^{\circ}C$. The rate of heating was $10^{\circ}C/min$. and the sample was soaked at $500^{\circ}C$ for 3h more. Phosphoric acid-activated carbons MP50, MP75 and MP100, respectively, were washed with 5% NaOH, then with distilled water until the pH of the washed solution was near to 7. The product were dried at $110^{\circ}C$ to a constant weight and were then stored in well closed bottles.

Impregnation ratio was defined as
impregnation ratio (w%) = weight of H_3PO_4 added/weight of dried maize
stalks [100]   (1)

MC500, was prepared by carbonization of the ground maize
stalks at 500°C for 3h. An additional sample, MS700, was prepared by
single-step steam pyrolysis as proposed by Gerogova et al. [**Gerogova et
al. (1996)**]. where maize stalks was directly carbonized and activated
simultaneously for 2h at 700°C. Products were dried at 110°C for 24 h in
a thermostatically controlled oven then stored in dry clean and well-
closed bottles.

The surface pH values of the aqueous suspensions of the prepared
carbons were measured as follows: 1 g of the dry, powdered carbon
sample was mixed with 50 ml of CO2-free bidistilled water and allowed
to equilibrate by shaking overnight in a stoppered glass bottle. The pH of
the carbon slurry was determined using digital pH meter (PoPe model 1
No. 1501).

2. TECHNIQUES
2.1 Nitrogen adsorption

Nitrogen adsorption isotherms at 77K were measured using a
vacuum apparatus of the conventional type. Before carrying out
adsorption measurements, the carbon sample was out-gassed under a
reduced atmosphere of 10^{-4} Torr at 200 °C for 2h. Adsorption data were
analyzed by applying the BET equation besides both α and t methods.
Application of the BET equation leads to the estimation of the specific
surface area S_{BET}. The total pore volume (V_P,ml/g) was estimated from
the volume of liquid nitrogen retained near to the saturation vapor
pressure. From S_{BET} and V_P an estimate for the mean pore radius (r^-, nm)
was obtained, assuming cylindrical pores open at both ends, from the
empirical relation:

$$r^- (\text{nm}) = 2V_P(1000)/S_{BET}$$ (2)

Two additional independent methods were also applied to
analyze the nitrogen adsorption isotherms. the first method plots the
volume of gas adsorbed V_{ads} (evaluated as milliliters liquid of N_2), versus
the reduced isotherms values (α_S) determined on a standard non-porous

material as recently reported by Sellez-Perez and Martin-Marineze [**Sellez-Perez and Martin-Marineze (1991)**]. The second method plots the amount of gas adsorbed versus the multilayer thickness (t, $\mathring{A}$) measured on a standard non-porous carbon [**Lippens and deBoer (1965)**]. From each of both latter two methods, four parameters were obtained: the total specific surface area (S^{α}, S^{t}) were evaluated from the slope of the initial linear section connecting to the origin and from slope and intercept of the latter linear section we get the external or non-microporous surface area (S^{α}_{n}, S^{t}_{n}) and the micropore volume (V^{α}_{mic}, V^{t}_{mic}). The breaking point between the linear sections donates primary filling of micropores with pore width (W^{α}, W^{t}) equal to twice the value of α or t.

2.2 Thermal behaviour through themogravmetric analysis.

In order to have a better understanding of the pyrolysis process, the thermogravimetric analysis was performed for two samples, the raw maize stalks and for the same soaked in 50 wt% H_3PO_4 overnight and dried at 383k. An apparatus of the type Perkin-Elmer 7 series was used. Thermal analysis system was employed at a heating rate 10K/ min up 1273 K. The result displays both TG and DTG tracings.

2.3 FT-IR and X-ray diffraction

Fourier transform infrared (FT-IR) spectra were obtained using a Mattson 5000 spectrophotometer. Pressed potassium bromide (KBr) pellets at a sample/KBr weight ratio of 1:100 were scanned and recorded between 4000 and 400 cm^{-1}. The X-ray diffraction patterns were measured by using a Philips diffractometer (type PW 1390). The patterns were run with nickel filter-copper radiation ($\lambda=1.5405$ $\mathring{A}$) at 30kV and 10 mA with a scanning speed of 2° in 2 θ min^{-1}.

2.4 Scanning electron microscopy

The scanning electron microscope (SEM) was used to examine the surface of samples MC500, MP75 and MS700. For SEM examination, an apparatus of SEM-type Jeol JSE-T20 was used at a magnification of X=500.

2.5 Adsorption from solution

In these experiences, lead nitrate was used due to its nonhydrolyzable anion. A stock solution of 1000 mg/l of Pb^{2+} was prepared by dissolving Pb $(NO_3)_2$ salt (AR-grade) in 1000 ml of bi-distilled water. Different concentrations were prepared by dilution from this stock solution. 100 ml of Pb^{2+} aqueous solution were pipetted into stoppered glass bottles and 50 mg of powdered carbon sample were added in each bottle. These bottles were shaken for 24 h at 25°C. The residual metal ions concentrations of the supernatant solution was measured by atomic absorption spectrometer using an apparatus of Perkin-Elmer model 2380. Pb^{2+} adsorption isotherms were constructed by plotting the amount of lead ions adsorbed, X_m (mg/g), as a function of the equilibrium Pb^{2+} concentration, Ce (mg/l). Analysis of Pb^{2+} adsorption isotherms were performed by applying the Langmuir and Freundlich equations. The Langmuir equation is given as

$$C_e/X_e = 1/K_L X_m + (1/X_m).C_e \qquad \text{Langmuir eq. (3)}$$

Where C_e and X_e are the amounts of substrate (Pb^{2+}) in solution and on solid (carbon). Linear plots of (Ce/ X_e) vs Ce gives X_m and K_L; X_m is the amount of Pb^{2+} adsorbed corresponding to monolayer coverage (mg/g) and K_L is the Langmuir constant (cm^3/m mol). On the other hand, the empirical linearized form of the Freundlich equation can be written as

$$\log X_e = \log K_F + (1/n) \log C_e \qquad \text{Freundlich eq. (4)}$$

Where n and K_F are the constants for a given solute-adsorbent system. which are obtained from a linear plot of log X_e vs log Ce.

3. RESULTS AND DISCUSSION

3.1 Textural properties

Table 1 summarizes the porosity and texture parameters of the investigated carbons samples as derived by both BET and Langmuir equations as well as α_s and t- plots. The data listed in Table 1 reveals that phosphoric acid-activated carbons exhibited S^α values between 379 and 926 m^2/g and total pore volume between 0.404-0.707 ml/g. Evidently, MP75 measured the highest S^α and V_P values. MP100 measured the

lowest S_{BET} and V_P values which may be attributed to the blockage of the developed pores and/or by the residual phosphates acting as a skin which may protect the chars complete carbonization. Thus one can say that the acid impregnation ratio of 75 w% achieved the highest effect on the precursor despite it is not sure that this is the optimum acid-concentration; that is may need to study additional concentrations.

Although both MP50 and MP100 samples produced low developed porosity carbons compared with MP75 carbon, yet, different reasons might raised here. MP50 prepared with 50 w% H_3PO_4 is weak acid-concentration. While MP100 sample prepared with the highest impregnation ratio, 100 w%, yielding the lowest developed porosity with S^a of 379 m^2/g and V_P of 0.404 ml/g. The mechanism that may be expected here based on the opposite effect occurs at high acid concentration. Because the excess of acid, during calcination, still rest as PO_4^{3-} and acts as a protective layer or skin that might protect the charred material from pyrolysis action and thus leading to this drastic decrease in the pore structure. Another mechanism may be expected here and based on the high acid-impregnation ratio yields a quantity of phosphate derivatives under pyrolysis action still rest in the carbon matrix even after repeated washings. This may lead to partial pore-blocking and pore-constrictions causing the inaccessibility of a part of the total pore system to nitrogen molecules **[El-Hendawy(2005); Jagtoyen and Derbyshire (1998) and El-Hendawy (2006)]**.

These observation are consistent with the proposition that phosphoric acid appears to act as a catalyst which promotes bond cleavage reactions with the cellulosic units, as the major component in the maize stalks, (equation 5). The bond cleavage reactions are proceed via cyclization and condensation processes to form phosphate and polyphosphate bridges that connect and crosslink biopolymer fragments. At low temperatures the formation of phosphate esters on cellulose side chains and crosslinking are expected to occur (equation 5); while at higher temperatures , as the case here, the phosphate linkage become thermally unstable and leaves the matrix as poly-aromatic clusters through elimination of most of the H_3PO_4 as reported latter in equation 6 **[Jagtoyen and Derbyshire(1998)]**. The traces of phosphates rested in the acidic carbons were confirmed by IR thereafter.
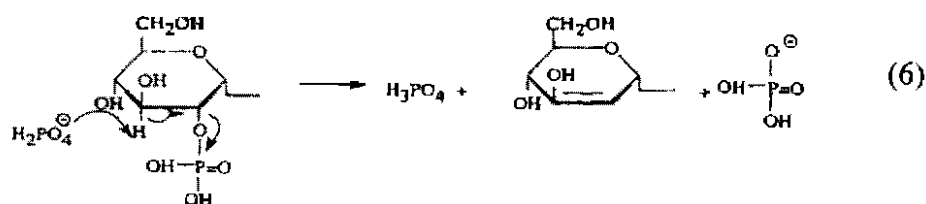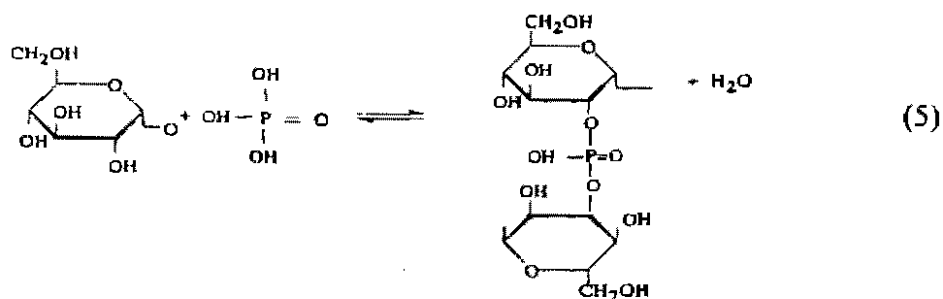
$$(5)$$

$$(6)$$

One step steam pyrolysis proved to be an effective procedure to obtain an activated carbon; MS700 exhibited S^{α} of 708 m^2/g and a total pore volume of 0.606 ml/g. A simple mechanism proposed here supposes that steam at ~ 700 °C may act as a cleaning agent getting rid of most of the disorganized and less-ordered carbon components which formed during carbonization, as CO and CO_2, leading to creation of porosity. This is confirmed, thereafter, by some spectroscopic tools in this study. Also this gains this method an additional importance where it conducts without chemicals simultaneously in one step.

The BET-C value is often quoted as providing a suitable guide to the applicability of the BET method. Table 1 indicates that their values greater than 150 in most cases, implying that the method is not wholly-reliable [Warhurrst et al. (1997)]. In addition, both S^{α} and S^t values are comparable than the S_{BET} ones. This may be attributed to the narrow range of relative pressure in which the BET method is applied. This takes us to believe that the S^{α} are the true values for the surface area here where α_s method cover a wide range of the relative pressure.

Fig. 1 shows the nitrogen adsorption isotherms at 77K. The isotherms are mixed type of type 1 and type IV according to BDDT classification [Brunauer et al. (1940)] with limited closed hysteresis loops at higher relative pressures indicating developing both meso- and microporosity. Moreover, the absence of a plateau and continuous rise of α_s-plots (Fig.2) indicates that a considerable fraction of the surface is located in mesopores. This may explain the high values of the external surface areas S_n^α and S_n^t as evaluated from both α and t-plots (Table 1). One interesting observation was derived from Table 1 (column 5) where r values for both acid and steam carbons are ranged between 1.565-2.290 nm. This supports the conclusions that the mesoporosity was developed sometimes by both chemical and physical activation schemes.
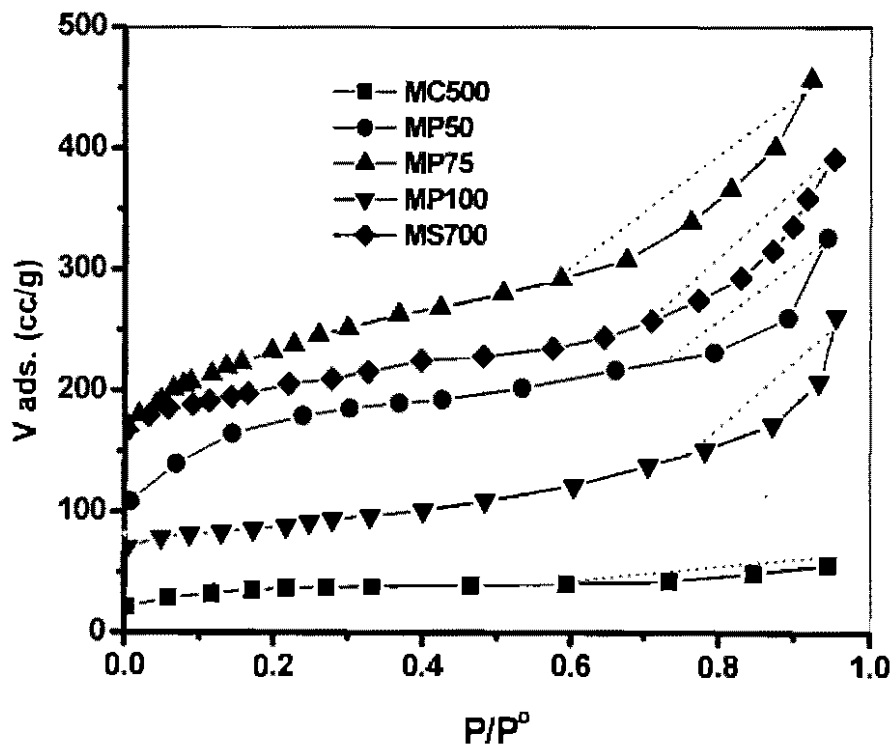

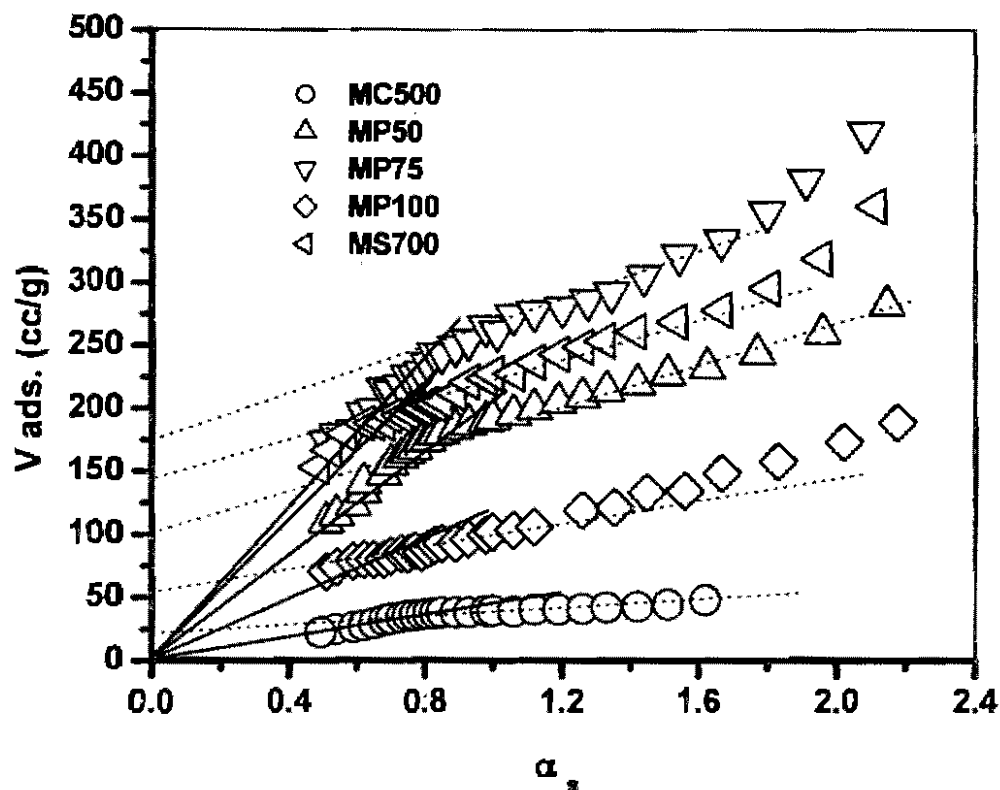**Fig.(1):** Adsorption isotherms of N_2/77K on the investigated carbons.

Fig.(2): α_s-Plots for $N_2/77K$-adsorption isotherms of the investigated samples.

3.2 Comparison of the external surface of the resulting carbons

The scanning electron micrographs of the surface appearances of both H_3PO_4 activated carbon MP75, and steam pyrolysis activated carbon MS700, compared with the char MC500, are shown in Fig. 3 (a,b,c). It can be seen from the micrographs that the external surfaces of all these carbons are in the form of cavities, especially for the carbons activated with H_3PO_4. The cavities on the surface of the H_3PO_4-carbon resulted from the evaporation of this chemical reagent during carbonization, leaving the space previously occupied by the reagent. The scanning electron micrograph of carbon MS700 suggests a relatively ordered structure. presumably derived from removing of the less-ordered

components that may present in the lignocellulosic structure leading to a contraction and twisting as thermal activation occurs. This could be taken as an evidence that steam acts as cleaning agent to all disorganized components as proposed in the previous section. The external surface of the char, MC500, is more intact than that of the other two samples. However, there are numerous small pits distributed over the surfaces of the three samples, indicating the occurrence of carbon gasification on the external surface during carbonization.
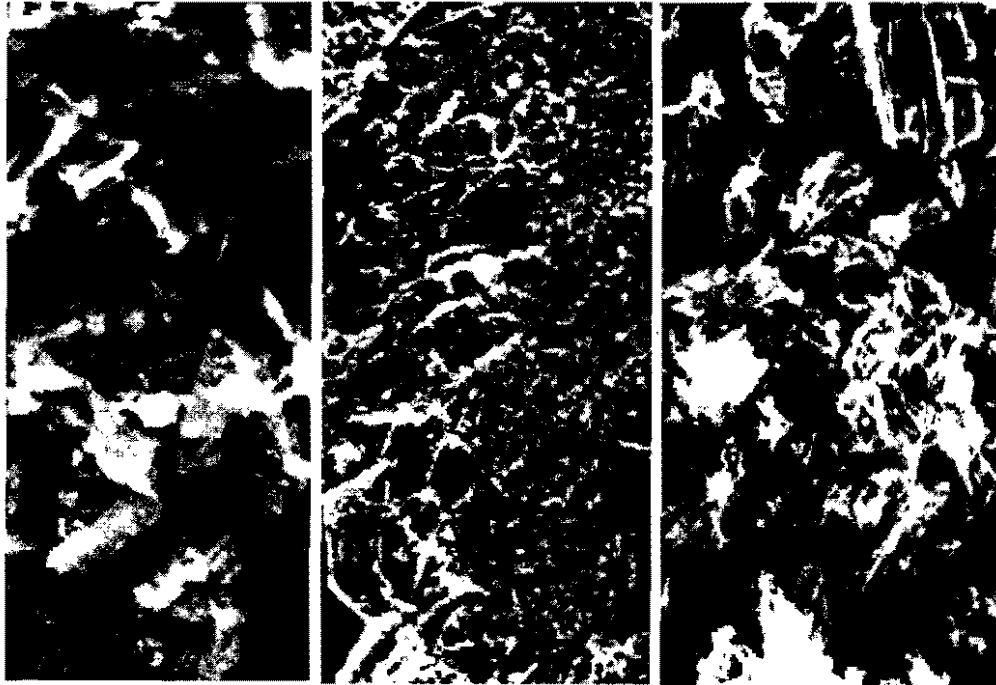
(a) MC500 X=500   *(b) MP75 X=500*   *(c) MS700 X=500*

Fig.(3): Scanning electron micrographs at a magnification of X= 500: (a) char MC500. (b) phosphoric acid-activated carbon, MP75 and (c) steam-activated carbon, MS700.

On the other hand, the X-ray diffraction pattern depicts additional findings in this context. Fig. 4 shows the XRD profiles of MS700, together with that of MC500. There were no diffraction peaks corresponding to MC500 sample indicating amorphous structure. On the other hand, a broad band, as a halo, at $2\theta = 26^\circ$ was appeared in the profile of MS700. This indicates increasing regularity of crystalline structure and ordering, which will result in a better layer alignment [**Lua & Yang (2004) and Bansal et al. (1988)**]. It might be due to the relatively higher activation temperature, $700^\circ C$, at which steam sample was prepared. This is in agreement with the well-known previously, in a crystalline carbonaceous structure, such as graphite, the interlayer distance between two adjacent carbon sheets is 0.335 nm. In this study, the peak at $2\theta = 26^\circ$ corresponds to an interlayer distance of 0.338 nm, which is quite similar to that of graphite. These observations, together with the SEM experiment, leads to the conclusion that a high activation temperature burns off the disorganized components, resulting in a reduction of the amorphous structure.

3.3 Weight loss behaviour during carbonization

The weight loss behavior during carbonization of maize stalks, MS, and after treatment with H_3PO_4 was studied by thermogravimetric analysis (TGA) of the parent and treated samples (Fig. 5). Although the tracings of both MS sample and treated one include three stages of weight loss, yet, significant modifications in the weight loss as a consequence of H_3PO_4 impregnation were observed. In the early stage of carbonization between 100-300 $^\circ C$, the behavior of both samples recorded significant differences where the weight loss of the raw material reach up to 81.38 % while still not exceed than 37.59 % in the treated sample. This clearly indicates that the maize stalks lose the significant part of their weights in early stage, and thus the main peak for weight loss was observed at 298 $^\circ C$. The early evolutions of the volatiles can be attributed in the raw material to moisture in addition to various volatile hydrocarbons. While it can be ascribed in the treated sample to the bond cleavage reactions caused by hydrolysis of the lignocellulosic material during H_3PO_4 impregnation [**Jagtoyen & Derbyshire (1998) and Molina-Sabio (1995)**]. The bond cleavage was subsequently followed by

extensive cross-linking at higher temperatures, leading to bonding of otherwise volatile materials into the carbon product and thus suppressing the evolution of tars and increasing the carbon yield [Li-Yeh & Teng (2000)]. This may explain the retardation of the major weight loss stage in the treated sample up to higher temperatures > 700 °C. The evolutions at these higher temperatures are mainly attributed to the decomposition and/or vaporization of polyphosphoric acids such as H_3PO_4, $H_4P_2O_7$, and $H_5P_3O_{10}$ [Molina-Sabio et al. (1995) and Li-Yeh & Teng (2000)].
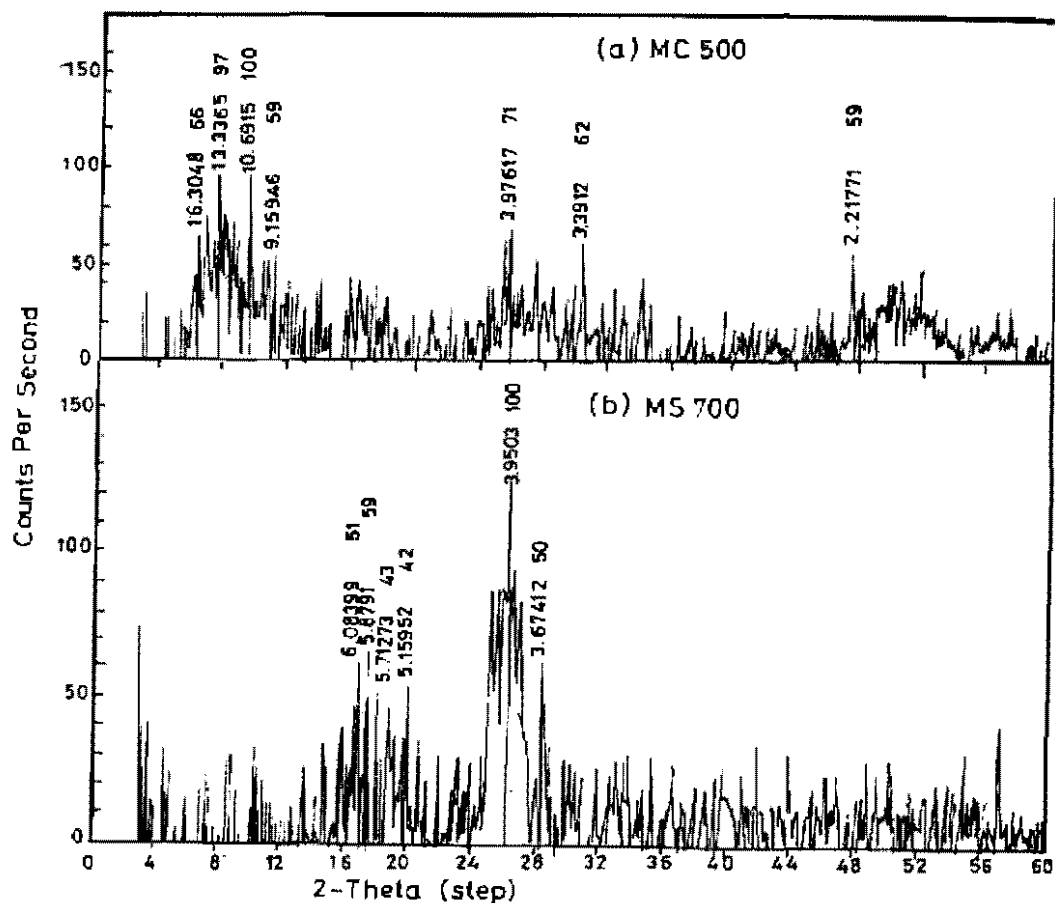

Fig. (4): X-ray diffraction profiles: (a) char MC500 and (b) single step-steam activated carbon prepared at 700°C, MS700.
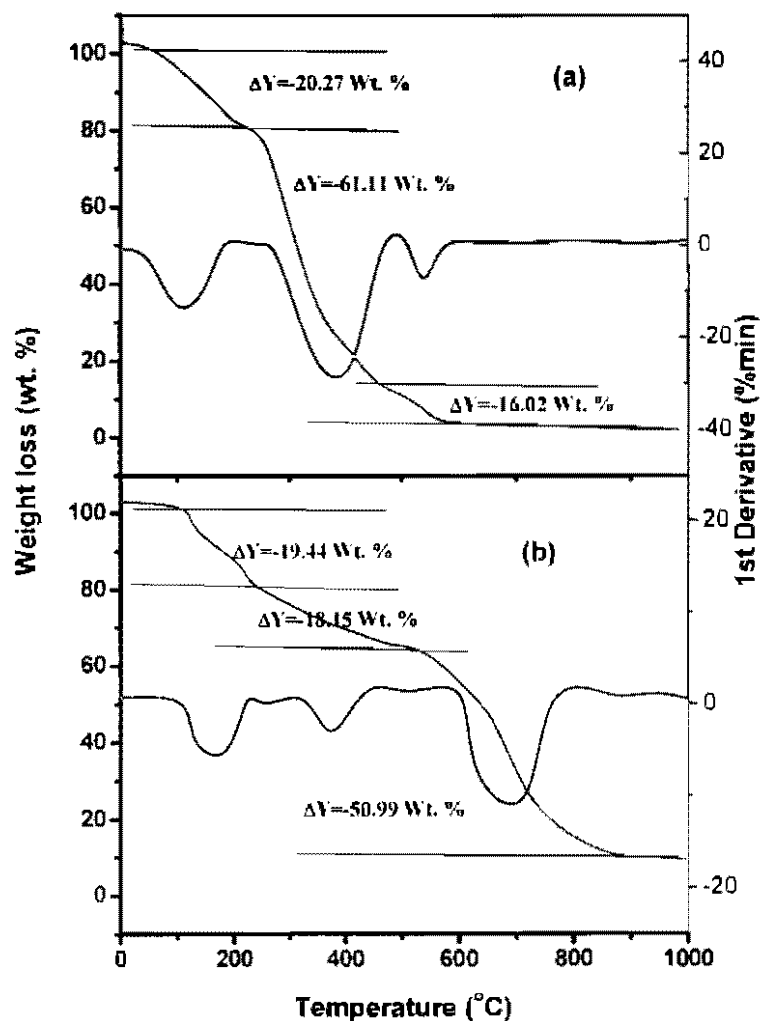
Fig. (5): Thermal behavior (TG and DTG curves) for: (a) raw maize stalks and (b) 1:1 w/w H_3PO_4-treated ones.

3.4 Surface chemistry

The Fourier transform infrared (FTIR) spectra of the char and activated carbons prepared by chemical and thermal activations (MC500, MP75 and MS700, as representative samples) are shown in Fig. 6. All the carbons showed broad bands at ~ 3450 cm^{-1} which may be due to hydrogen bonded of –OH stretching vibration that arise probably from the interaction between the adsorbed water molecules from environment and OH groups on the carbon surface [El-Hendawy (2006) and Guo & Lua (2003)]. The acidic activated carbon, MP75, spectrum displayed the following bands

1737 cm^{-1} C=O stretching vibration in ketones, carboxylic acids

1640 cm^{-1} C=O stretching vibration in quninones

1505 cm^{-1} C=C stretching vibration in aromatic rings.

1219 cm^{-1} C-OH stretching vibration in phenols

1590 cm^{-1} C=C stretching vibration in olefinic double bonds.

The bonds at 1455, 1137, 980 cm^{-1} may be ascribed to R-aryl, P-O-C stretching in phosphate groups and P=O, respectively. However, most of these functional groups are acidic in nature, one of the important observation here is the appearance of phosphates bands that might suggest the presence of phosphate residues in the carbon matrix even after intensive and repeated washings. On the other hand, two characterized observations are observed in the FTIR spectrum of MS700 sample. First, a relative decrease was observed in the band intensities that may be attributed to the relatively higher temperature at which steam pyrolysis was prepared which enables the decomposition of the most functionalities on the carbon surface. Second, the appearance of the band at 2355 cm^{-1} that may be ascribed to C=O stretching vibration was probably due to ketene [El-Hendawy (2006); Guo & Lua (2003) Bansal et al. (1988) and Patrick et al. (1995)]. This band always signifies and presents in most thermal activation carbons. In the char, MC500, spectrum the appearance of the band at 870 cm^{-1} could be assigned to C-H out of plane bending vibration. The bands at 1740 and 1539 cm^{-1} could be ascribed to the formation highly conjugated C=O stretching, C-O stretching in carboxylic groups and carboxylate moieties, respectively. It is worth noticed that in all three spectra. the main oxygen groups are

present which played thereafter the major role in Pb^{2+} adsorption from aqueous solutions.
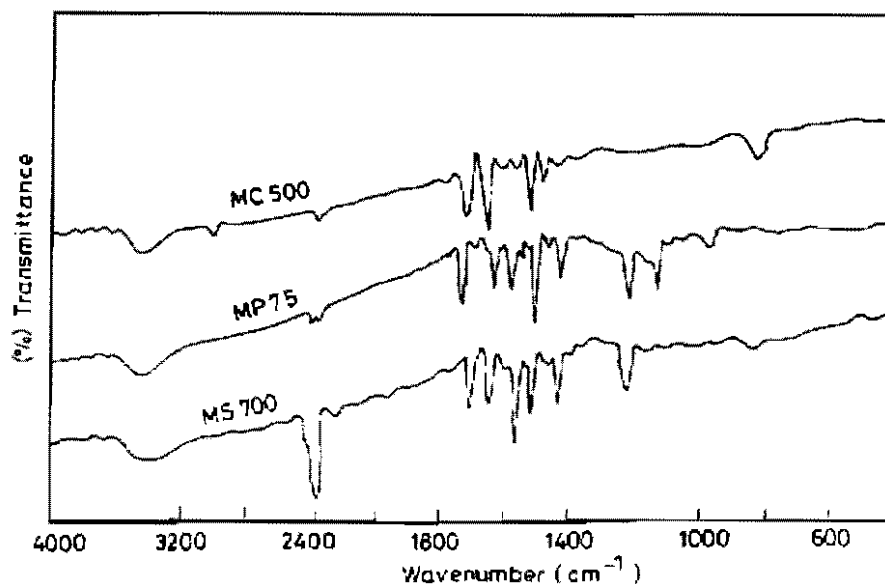

Fig. (6): FTIR spectra for some selected samples.

3.5 Adsorption from solution

It has been established that the adsorption from solution depends on the pH of the carbon surfaces. For this reason we reported the values of pH slurry for the carbon investigated in Table 1. Pb^{2+} adsorption isotherms are shown in Fig. 7. They might be included in the third type H according to Giles classification [**Giles et al. (1960)**]. This indicates that the solute (Pb^{2+}) has high affinity to interact on the solid (carbon) surface. These isotherms fit the Langmuir equation up to Ce ~ 60 mg/l.. The behaviour of the prepared carbons in this adsorption process should be explained not only on the basis of their textural properties but also on their surface chemical nature and their ion exchange capacities. Table 2 reveals that X_m with relation to Pb^{2-} adsorption ranges from 57 to 358 mg/g and decrease in the order MP75> MS700>MP50> MP100>MC500, this sequence appears in complete agreement with S^u sequence. The constants of the Freundlich and Langmuir equations n. K_F and K_L constants for a given solute-adsorbent system in addition to a normalized standard deviation SD and correlation coefficient R are given in Table 2.
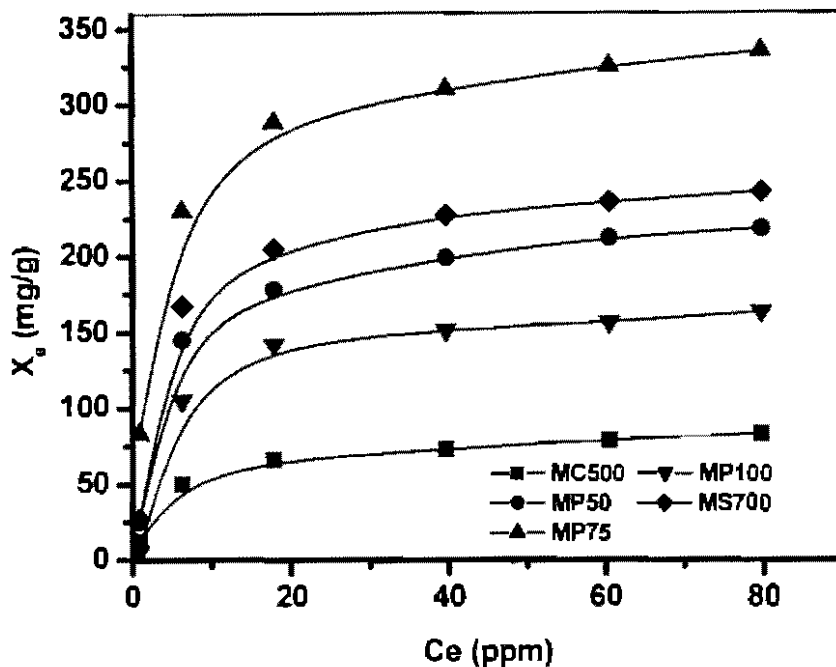
Fig. (7): Pb^{2+} adsorption isotherms for the investigated carbons from aqueous solution (at 25 °C).

Generally, it has been previously reported [**Ferro-Garcia et al. (1990)**], concerning the Pb^{2+} adsorption, that from the whole range of pore radii just ulter-micropores (less than 0.8 nm in diameter) should be inaccessible to Pb^{2+}, therefore, the accessible surface area corresponding to supermicro-, meso- and macropores would represent the effective fractions of the surface area for removing Pb^{2+} from aqueous solutions. Thus, the high lead adsorption capacity of those activated carbons might be due to the fact that most of the carbons studied have great values of the mean pore radius, r, ̄ ranged between 0.940 to 2.290 nm (Table1), i.e. located above the ultramicropore range. Evidently, these carbons have big fractions of their surfaces which are available and accessible to Pb^{2+} as hydrated ions ($Pb^{2+}aq$) in aqueous solutions. This can explain the higher values of surface areas covered by lead ions, S^{Pb2}.Which are, sometimes, comparable to their counterparts measured by nitrogen, S_N^{α} (Table 2).

Although, carbon MP100 reported low values of pH and S_{BET}, yet, it uptaked considerable amount of Pb^{2+} reach up to 151 mg/g. This is in contrasts with the previously reported [Brain et al. (1996)] that the higher basic surface, the higher metal adsorption. The explanation raised here might be due to the fact that this sample was prepared at the highest acid-impregnation ratio. The excess quantities of acid converted into phosphates derivatives under the pyrolysis action that may rest on the carbon surface and act as active centers capable to sequestrate Pb^{2+} from aqueous solutions. This observation, together with the appearance of phosphate-IR band, that makes this conclusion was more acceptable as confirmed in our preliminary experiment [El-Hendawy (2005)]. On the other hand, steam pyrolysis carbon resulted in a reasonable value of lead adsorption, X_m of 253 mg/g; this was assumed to be related to two facts, first, the basic surface nature, pH of 8.3, second, the highest opened pore structure, r^- of 1.763 nm. Consequently, they will allow maximum penetration of the lead hydrated ions, providing easy transport to meso- and macropores and thus, facilitates the internal pore diffusion to the adsorption basic sites through ion exchange. This suggests that adsorption of Pb^{2+} by ACs is initially by surface precipitation followed by ion exchange and surface complexation of Pb^{2+} at carbon surface. Above mechanisms are very much in agreement with Fig. 7. As presented in the table, high values of correlation coefficient R for both Langmuir and Freundlich data for all adsorbents indicates good Pb^{2+} uptakes for all carbon studied from aqueous solutions.

Table (I): Textural parameters as evaluated from the nitrogen adsorption isotherms at 77K.

Sample Notation	pH slurry	S_{BET} (m²/g)	V_P (ml/g)	$\bar{r}$ (nm)	C	α_s - parameters				t- plot Parameters			
						S^α (m²/g)	S^α_n (m²/g)	V^α_0 (ml/g)	w^α_0 (Å)	S^t (m²/g)	S^t_n (m²/g)	V^t_0 (ml/g)	W^t (Å)
MC500	7.4	108	0.051	0.940	699	128	24	0.047	7.80	132	28	0.056	7.72
MP50	5.8	594	0.505	1.70	978	610	185	0.195	8.70	633	177	0.196	8.96
MP75	5.1	903	0.707	1.565	45	926	263	0.270	8.30	918	266	0.278	7.32
MP100	4.3	353	0.404	2.29	133	379	162	0.065	6.10	374	140	0.079	6.75
MS700	8.3	687	0.606	1.763	650	708	154	0.225	6.30	693	159	0.227	6.17

Table (2): Adsorption parameters of Pb^{2+} for the investigated carbons.

Sample Notation	Langmuir Parameters					$S Pb^{2+}$ / S^{α}_N	Freundlich Parameters			
	X_m (mg/g)	S^{Pb2+} (m^2/g)	K_L (L/g)	R	SD		n	K_F (L/g)	R	SD
MC500	57	83	0.1103	0.9991	0.0074	0.640	5.339	68.80	0.9993	0.00221
MP50	243	356	0.1280	0.9997	0.0031	0.583	6.775	114.74	0.9970	0.00357
MP75	358	525	0.1740	0.9990	0.0023	0.617	10.080	216.00	0.9835	0.0058
MP100	151	221	0.1190	0.9967	0.0085	0.583	7.400	147.13	0.9655	0.01165
MS700	253	371	0.1410	0.9991	0.0052	0.410	7.650	128.82	0.9984	0.0023

S^{Pb2+} = accessible surface areas covered by Pb^{2+}, R = correlation coefficient, SD= stander deviation.

CONCLUSIONS

- Maize stalks appear to be a promising precursor for the production of moderate to good activated carbons by one step activation whichever with phosphoric acid or with steam.

- S_{BET} and V_P can be altered by increasing the ratio of acid to precursor at $500^\circ C$ and a wide spectrum of pore structures are possible to obtain upon variations in the acid impregnation ratio or the activation scheme.

- Phosphoric acid appears to act as acid catalyst to promote bond cleavage reactions to form crosslinked new biopolymer fragments derived from the insertion of phosphate groups with cellulose molecules. Phosphoric acid modified the surface chemistry of obtained acidic-carbon due to the formation acidic functional groups and cavities on the carbon surface as confirmed by FTIR and SEM studies. Moreover, it is associated with a decrease in tar evaporation leading to a sharp increase in both carbon yield and carbon thermal stability up to higher temperatures as appeared by TGA studies. In this context, different mechanisms for acid and steam activations were proposed.

- One step steam pyrolysis proved to be an effective procedure to obtain an activated carbon from the same precursor. In addition to save energy, chemicals and time, it yielded a carbon of reasonable porosity reach up to S_{BET} 687 m^2/g.

- All investigated carbons appeared to possess high lead adsorption capacities from aqueous solutions which ascribed, in major, to their high values of the accessible surface areas available for Pb^{2+} as hydrated ions in aqueous solutions; viz have r$^-$ values >0.8 nm. In addition, carbon porosity, surface chemical nature, carbon surface-pH and ion exchange mechanisms were found to be effective contributed factors. The results indicate that maize stalks activated carbons could be employed as a low cost alternative to commercial activated carbons and appeared as high quality AC in the removal of heavy metals from aqueous solutions.

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تحضير الكربون المنشط من عيدان الذرة باستعمال حمض الفسفوريك
وتطبيقاته فى ازالة العناصر الثقيلة

عبد الناصر عبدالله الهنداوى

قسم الكيمياء الفيزيقية ــ المركز القومى للبحوث

أضحى تحضير الكربون المنشط من الموضوعات الحيوية والهامة من الناحية
البيئية والأقتصادية. وفى هذا البحث تم استعمال عيدان الذرة ــ وهى مخلف زراعى
لايستفاد منه ــ فى تحضير عدد من عينات الكربون المنشط وذلك باستعمال حمض
الفسفوريك بتركيزات مختلفة ثم بالمعالجة الحرارية فى وجود غاز النتروجين. تم توصيف
هـــذه العينات بقياس قــدرتها علـى امــتزاز غــاز النتروجــين عـنـد درجــات
الحــرارة المنخفضة (−196 درجة مئوية) ثـــم بتحليل منحنيات الامتزاز بطرق عديدة مثل
الـ BET، Langmuir ، α_s, t- وتم التحقق من أن العينات قيد البحث عالية ومتنوعة
المسامية ويغلب عليها النوع ميـــزو.

فى سياق التوصيف الدقيق للعينات المحضرة تم استعمال جهاز التحـــليل الحرارى
و الميكرسكوب الالكترونى وجهاز الأشعة تحت الحمراء وأمكن بذلك معرفة السلوك
الحرارى لعينات الكربون و معرفة شكل السطح ونوع المجموعات الوظيفية عليه.

يعتبر الرصاص من أخطر الملوثات على المستوى العالمى، وقد برهنت العينات قيد
البحث على قدرتها الفائقة على ازالة هذا العنصر الثقيل من المحاليل المائية بنسب وصلت
الى 358 ملجرام رصاص لكل جرام كربون. وقد تم التطرق لآلية الامتزاز لهذا
العنصر وللعوامل المؤثرة فيه.