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The effect of temperature and impregnation ratio on the active carbon porosity

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ABSTRACT

Three active carbons were prepared starting from Algerian date pits by chemical activation with the H_3PO_4, $ZnCl_2$ and by the method combined in the presence of $ZnCl_2/CO_2$. A systematic study of certain parameters (temperature of activation and impregnation ratio) was undertaken. The active carbons obtained were followed by the evaluation of the yield and the physisorption of nitrogen at 77 K. It was shown that the preparation of activated carbon by H_3PO_4 and $ZnCl_2$ requires relatively moderate temperatures (500–600°C) while the combined method is rather favored at higher temperatures (800°C). The variation of the impregnation ratio revealed that the active carbons obtained have different porosities. Indeed, the prepared carbon by chemical activation with the phosphoric acid is made of mesoporous structure whereas the carbon prepared by $ZnCl_2$, shows a very high ratio of microporosity (90%). This difference in porosity is directly related to the proper activation mechanism of each chemical additive. The study of the evolution on a specific surface of the prepared carbons with various impregnation reports/ratios shows that an increase in the impregnation ratio, improves the specific surface when H_3PO_4 is used, contrary to the other agents where the surface reaches a certain value then decreases again. In general, a high rate of impregnation led in all cases to a more marked opening of porosity and particularly in presence of H_3PO_4. This results in the development of a less specific surface, compared with the prepared carbons by $ZnCl_2$ and $ZnCl_2/CO_2$. The elaborate active carbons have very interesting textural characteristics and can have various applications.

Keywords: Activated carbon; Chemical activation; Specific surface; Pore volume

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1. Introduction

Mesoporous or macroporous carbons have been widely used as catalysts supports, battery electrodes, superelectric capacitors and adsorbents for large molecules or adsorption from solutions [1–3]. However, commercial activated carbon is usually composed of micropores with limited mesopores and macropores. Thus, it is essential to modify the pore structure of commercial activated carbon and increase its mesopore content for matching such applications.

A variety of methods for the preparation of mesoporous carbon were reported [4]. Currently, research is directed towards elaborating mesoporous active carbons of large specific surfaces with a mesoporous fraction of more than 80% on the total porous volume. They are obtained starting from microporous commercial active carbon, of polymer and phenolic resins by impregnation with glucose followed by a carbonization and activation to the carbon dioxide [5,6]. However, all these processes

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are expensive compared to the method of preparation quoted by Zhonghua Hu et al. [7]. Indeed, it showed that mesoporous active carbon can be obtained at a lower cost by chemical impregnation in $ZnCl_2$ with 800°C followed by activation with CO_2. This technique combining the chemical method ($ZnCl_2$) and the physical method (CO_2) helps to widen the pores allowing the conversion of the micropores into mesopores. However, activation with the phosphoric acid remains preferable not only because the extraction of carbon is easier, but also because $ZnCl_2$ poses problems of contamination by zinc with the environment.

2. Material and methods

2.1. Preparation of active carbon by chemical activation

Date pits (Deghlet Nour) coming from the Algerian south are washed, dried in the oven with 110°C during 12 h and then crushed. After sifting, the fraction of diameter lower than 100 μm is intended for activation in the presence of phosphoric acid, whereas that ranging between 0.5 and 1 mm is impregnated with zinc chloride.

2.1.1. Activation with the phosphoric acid

The powder of the date pits is mixed with phosphoric acid at a ratio of 2 ml/g. The mixture is carried to reflux for 2 h [8] — time considered sufficient so that the phosphoric acid can occupy the entire surface offered by the substratum. The mixture is then placed at the temperature wanted in a programmable pipe shaped oven, rising the temperature of 5°C/min. On the basis of this general protocol, we will vary certain parameters such as the temperature of activation or the concentration of the phosphoric acid allowing the variation of the report/ratio of impregnation. Activation, in all cases is maintained during 1 h. At last, carbons obtained are washed until constant pH.

2.1.2. Activation with zinc chloride

The impregnation is carried out with various impregnation ratios (mass of $ZnCl_2$ brought back to the mass of the lignocellulosic precursor). The mixture is triturated during 10 min in order to allow its homogenization, then it is brought up to a temperature varying between 500 and 800°C, with a heating rate of 5°C/min under nitrogen flux, in a programmable pipe shaped oven. Once the desired temperature reached, it will be maintained during 1 h. The active carbon obtained is then washed with the hydrochloric acid 0.1 N for 3 h, and then rinsed with distilled water until the test with silver nitrate on the filtrate proves to be negative.

2.1.3. Activation combined with $ZnCl_2$ CO_2

With the aim of improving the mesoporosity we proposed to carry out mixed activation according to the protocol of reference [9]. Thus, the particles whose diameter lies between 0.5 and 1 mm are impregnated in $ZnCl_2$ with various mass reports/ratios. This report/ratio varies from 100 to 300%. Once the mixture dehydrated in the oven with 110°C during 12 h, it is subjected to a rise of temperature of 10°C/min until 800°C under an inert gas flux with a flow of 20 l/h. When the temperature is reached, the nitrogen is replaced by CO_2 and the activation is maintained during 1 h. The later stage of rinsing being the same one as that was quoted previously.

3. Results and discussion

3.1. Effect of the activation temperature

3.1.1. Solid yield

It is initially suitable to note that the time of activation is maintained during 1 h and the report/ ratio of impregnation is 1 g/g for the prepared carbons by activation in $ZnCl_2$, and of 2.91 g/g for those impregnated with the H_3PO_4. Generally, for the three methods of activation employed, the increase in the temperature of activation lowers the active carbon output as shown in Fig. 1.

Nevertheless, it is useful to signal that the yield does not fall under 18%. The reduction in the yield represents the increase in the loss of mass, which is due to various reactional mechanisms taking place between lignocellulosic derivatives and the chemical agent. When $ZnCl_2$ is employed in chemical activation in the temperature range 500–800°C, the loss of mass is more important than in other methods [10,11]. Around 400°C, the precursor would have already lost all volatile material such as monoxide and the carbon dioxide under the effect of carbonization. More than this loss, we also suppose that between 430 and 500°C, $ZnCl_2$ is entirely dehydrated from water molecules taken by the precursor during the first stage of thermal degradation [12]. Also $ZnCl_2$ takes off the hydrogen and

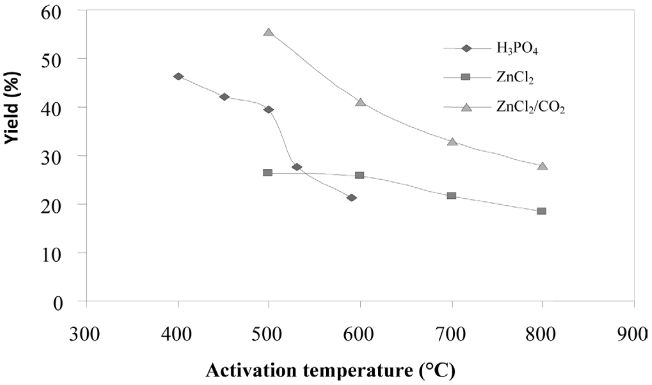

Fig. 1. Effect of the activation temperature on the active carbon yield. First, the yield η are classified as follows: η ($ZnCl_2$) < η (H_3PO_4) < η ($ZnCl_2/CO_2$).

oxygen atoms belonging to the carbonaceous structure of the material itself, to form water molecules.

At the low temperatures, activation with the H_3PO_4 led to active carbon with yield higher than the preceding case. When the temperature of activation passes from 400 to 500°C, the yield drops only from 46.4 to 39.4% whereas starting from 500°C, the reduction is much more important and the yield reaches 21.3% with 590°C. Indeed to temperatures lower than 500°C, the H_3PO_4 limits, by establishing a barrier formed of tar and other liquid material like the acetic acid and methanol. In this case, the conversion of the precursor into carbon is more important than that obtained with activation in $ZnCl_2$. It was established [9] that the barrier formed by polyphosphated species leads to a quite rigid matrix. The fact that the yield decreases considerably nearby 590°C shows that the structure (cross-linked structure) reached its resistance limit and the division of the bonds is accelerated under the effect of the temperature by decreasing the output more.

As for combined activation, the yield remains more important than in the two preceding cases that suggests that the loss of mass is less in this temperature range. Indeed, the essence of the volatile matter is released at temperatures lower than the studied temperatures (around 400°C). Beyond and in the presence of CO_2, $ZnCl_2$ does not seem to react according to the same mechanism as when it is associated to an inert gas. Moreover, the basic structure is already acquired and a few losses are announced beyond 500°C.

3.1.2. Specific surface and pore volume

The evolution of specific surface according to the temperature of activation is presented in Fig. 2. Globally, the specific surfaces obtained by the method of BET are interesting.

Activation in $ZnCl_2$ develops more important specific surfaces presenting a maximum of 1322 m²/g at 600°C. Beyond this temperature, surface reduces. This change of the surface profile can be allotted to the fact that the boiling point of $ZnCl_2$ is at 732°C. Indeed, very few works were devoted to chemical activation in $ZnCl_2$ beyond 800°C [14,15]. However, this research has shown that to temperatures higher than the boiling point of $ZnCl_2$ (800°C) the carbonaceous materials can lead to carbons of very interesting surfaces.

Conventionally, chemical activation with $ZnCl_2$ is conduced in an inert N_2 atmosphere at 500–700°C. Most of the $ZnCl_2$ remains in the carbon during activation and is removed by washing after activation. In the present study it was found that replacement of N_2 with CO_2 in the soaking stage coupled with the high temperature used in the activation process resulted in release of a significant amount of $ZnCl_2$ as observed from the condensation on the quartz tube. This would have resulted in releasing of blocked pores and aided penetration of CO_2 into the adsorbent and further oxidation of the pore wall.

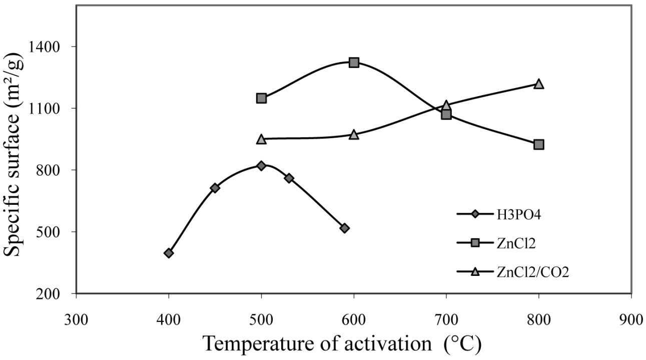

Fig. 2. Effect of the temperature of activation on the specific surface of active carbon.

$ZnCl_2$ activation has been known to increase the pore width as observed in the activation of olive stones [16] and in the activation of coconut shells and palm seeds [17]. Caturla et al. [15] attributed their observed pore widening at high $ZnCl_2$-to-raw material ratios to the fact that a significant faction of the $ZnCl_2$ would widen the pores due to large external localised decomposition. As observed in this study, $ZnCl_2$ is also known to increase yield due to the amount of tars produced [18].

The behavior of carbons obtained by combined activation ($ZnCl_2/CO_2$) not being identical developed surface increases continuously with the rise in the temperature and reached approximately 1220 m²/g with 800°C. Carbon dioxide seems to have a favorable and compensating contribution with the inhibiting action of $ZnCl_2$ when boiling from 732°C. Nevertheless, specific surface remains less important than that of the active carbons prepared by activation in $ZnCl_2$ under inert gas flux. This suggests that the carbons obtained by combined activation would be of a less microporous nature than in the preceding case.

As for the use of H_3PO_4, the activation process starts at lower temperatures. This justifies the less important mass loss. It is obvious that the development of porosity is at the origin of the evolution of the specific surface which presents a maximum of 820 m²/g at 500°C.

Table 1 shows the values of total porous volume (V_{totp}) correspondent at a relative pressure of 0.99; microporous volume $V_{\mu p}$ as well as the report/ratio $V_{\mu p}/V_{totp}$.

Mesoporous volume can be calculated by the difference between total porous volume and microporous volume. The results obtained indicate that the prepared active carbon by $ZnCl_2$ with 600°C is the most microporous. Its microporous volume is 0.66 cm³/g and represents a report/ratio $V_{\mu p}/V_{totp}$ of 81.4%. The small size of the $ZnCl_2$ or its hydrates will explain the small and uniform size of the micropores created. This is not the case for H_3PO_4 because there are no phosphoric acid molecules, but a mixture of molecules from the small H_3PO_4 and

Table 1
Evolution of porous volumes of active carbon according to their temperatures of activation

Chemical agent	Activation temp. (°C)	V_{ptot} (cm^3/g)	$V_{\mu p}$(cm^3/g)	$V_{\mu p}/V_{ptot}$ (%)
H_3PO_4	400	0.17	0.07	14.1
	450	0.72	0.38	52.7
	500	0.72	0.47	25.0
	530	0.74	0.19	25.5
	590	0.54	0.15	27.7
$ZnCl_2$	500	0.66	0.59	89.3
	600	0.81	0.66	81.4
	700	0.59	0.52	88.0
	800	0.51	0.45	88.2
$ZnCl_2$/ CO_2	500	0.84	0.47	55.9
	600	0.68	0.36	53.7
	700	0.61	0.33	54.2
	800	0.69	0.42	60.1

$H_4P_2O_5$ to $H_{13}P_{11}O_{34}$ in the proportion predicted by the liquid–vapor phase diagram for the P_2O_5–H_2O mixtures at the maximum temperature of the treatment, 450°C [19].

Contrary to the prepared carbon in $ZnCl_2$, this rate does not exceed the 60.1 and 25% respectively at the optimal temperatures of activation which are 800 ($ZnCl_2$/CO_2) and 500°C (H_3PO_4).

The reduction in the microporous volume of the prepared carbons by activation with the H_3PO_4 shows that, such carbons are of rather mesoporous structure, which justifies the lower value of their specific surface. The development of the mesoporosity with this chemical agent was largely discussed by many authors [20,21].

Indeed, the phosphoric acid changes in phosphated species and polyphosphated esters of big size. The species form a layer acting as a barrier which protects the porous structure of a possible excessive oxidation. At higher temperatures, the barrier breaks while leading to a lowering of porous volume. By its aggressive action, the phosphoric acid contributes to degrade the structure of the lignocellulosic derivative, and occupies a substantial volume. After extraction of the acid by wash, the empty pores appear broader than the previous cases.

3.2. Elementary composition

The effect of the temperature of activation was followed by the ultimate analysis of the active carbon. The composition of oxygen was determined by difference.

In all the cases, the nitrogen content is lower than 3% and that of sulphur with 1%. The rise in the temperature of activation decreases the hydrogen content and increases that of carbon, particularly for the prepared coals by $ZnCl_2$ in the presence of nitrogen or of carbon dioxide.

Table 2 shows the effect of the temperature of activation on the elementary composition of the prepared carbons.

3.3. Effect of the report/ratio of impregnation

It is convenient to underline that the activation of the date pits is carried out to 500; 600 and 800°C respectively with chemical agents H_3PO_4; $ZnCl_2$ and $ZnCl_2$ combined with CO_2, for 1 h. This section is thus devoted to the study of the rate of the impregnation ratio. This one is defined as being the report/ratio of the mass of the chemical agent and that of the powder or the grains of the date pits.

3.3.1. Yield

Fig. 3 shows that the increase in the report/ratio of impregnation lowers the active carbon yield, in particular

Table 2
Effect of the temperature of activation on the elementary composition of the prepared carbons

Chemical agent	Activation temp. (°C)	C (%)	H (%)	N (%)	S (%)	O (%)
Raw material		80.85	1.28	0.99	0.25	13.26
H_3PO_4	400	43.62	5.97	0.67	0.39	49.35
	450	41.45	5.92	1.19	0.30	51.14
	500	61.02	3.46	1.57	0.21	33.72
	530	51.73	1.46	0.25	0.19	46.37
	590	53.34	1.74	0.05	0.27	47.61
$ZnCl_2$	500	65.31	1.63	1.07	0.72	31.27
	600	69.37	1.11	1.22	0.73	27.57
	700	72.59	0.85	1.09	0.89	24.57
	800	85.25	1.33	2.72	0.68	10.02
$ZnCl_2$/ CO_2	500	60.70	1.05	0.86	0.52	37.57
	600	74.49	2.64	0.28	0.46	22.13
	700	87.77	0.81	0.18	0.65	10.59
	800	88.80	0.80	1.84	0.71	7.85

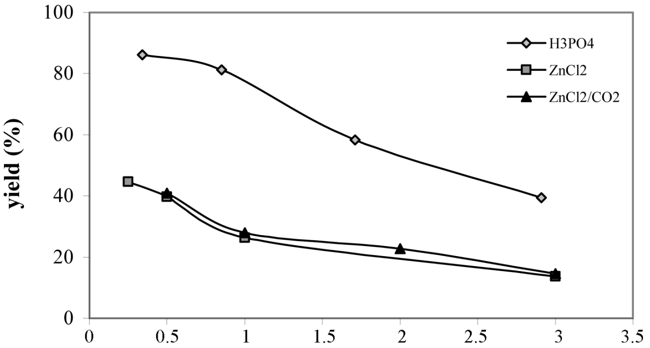

Fig. 3. Effect of the impregnation ratio on the yield of the active carbon prepared with various chemical agents.

Table 3
Evolution of porous volumes of active carbons according to their impregnation ratio

Chemical agent	X (g/g)	$V_{\mu p}$ (cm^3/g)	$V_{méso}$ (cm^3/g)	$V_{méso}/V_{p\ tot}$ (%)
H_3PO_4	0.34	0.19	0.026	12.0
	0.85	0.21	0.037	14.9
	1.71	0.41	0.092	18.3
	2.91	0.18	0.539	74.9
$ZnCl_2$	0.25	0.439	0.046	9.48
	0.50	0.741	0.022	2.99
	1.00	0.66	0.145	18.00
	3.00	0.58	0.308	39.58
$ZnCl_2$/ CO_2	1.00	0.62	0.060	2.82
	2.00	0.84	0.288	25.53
	3.00	0.46	0.123	21.10

when H_3PO_4 is employed like chemical agent. Indeed, this yield falls from 86.14 to 39.4% which is 46.74%. The prepared carbons with $ZnCl_2$ that is, under gas or inert carbon dioxide flux, adopt the same behavior concerning the evolution of their yield. The lowering of the yield is important in the range of 0.25–1 and attenuates itself between 1 and 3 g/g.

This reduction which testifies to a great mass loss can be due only to the degradation of the matrix of the lignocellulosic precursor, and to the opening of the pores.

3.3.2. Pore volume

In the case of activation in $ZnCl_2$ according to the traditional method and in the range of 0.25, 0.5, we record a simultaneous increase in the micropores and mesopores. Only mesoporous volume is lower than the microporous one. However, we notice an effect of competition between various porosities in favor of mesoporosity with the impregnation ratio $X = 1$. This suggests that at weak impregnation ratio the structure is not only microporous, but also homogeneous. These results are consolidated by those obtained by Molina et al. [12] showing that $ZnCl_2$ favors the creation of a rather microporous network. Once the rate of impregnation reaches 1g/g, microporosity decreases showing that there is on the one hand, the opening of the micropores in mesopores under the effect of the temperature and on the other hand, with the fact that the entities of $ZnCl_2$ become more voluminous (X large) accentuating further the hydrolysis and thus the swelling of the activating material.

As already indicated, activation in $ZnCl_2$/ CO_2 with various reports/ratios seems to have the same behavior as when one operates with $ZnCl_2$ alone. Nevertheless, in the range of 1.0, 2.0 the mesoporosity is more important than when the gaseous flux is inert suggesting that more than the role of $ZnCl_2$, the carbon dioxide allows the opening of the micropores created by the chemical agent in mesopores. For a rate of impregnation of 3, a curious fact and especially opposite to our expectations is raised, namely the reduction of the total porous volume of half compared to the impregnation ratio $X = 2$. The only plausible explanation to this behavior would be the fact that, the excess of $ZnCl_2$ blocks the evolution of porosity.

The rise in the impregnation ratio during the activation with the H_3PO_4 allows the development and the increase in microporous volume until a maximum of 0.41 cm^3/g for $X = 1.71$ g/g. Beyond this rate of impregnation, microporous volume decreases. As for mesoporous volume, it rises continuously from 0.026 to 0.539 cm^3/g, contrary to the volume of the micropores.

The rise of the real density highlights the real reduction in the volume of the material and consequently the creation of porosity and the widening of certain already formed pores.

4. Conclusion

Chemical activation of date pits with $ZnCl_2$, H_3PO_4 and $ZnCl_2/CO_2$ produces activated carbon with well-developed porosity and surface specific comparable with those of commercial products used as industrial adsorbents. It is found that the surface area and the nature of the porosity can be controlled by means of the experimental parameters.

Thus date pits are of interest as a precursor for the preparation of active carbons used in several domains. This is due to their advantageous characteristics such as mainly their very developed porous texture, great specific surface, consequently the capacity of adsorption and the thermal stability.

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