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Preparation and characterization of an activated carbon from a date stones variety by physical activation with carbon dioxide

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ABSTRACT

Activated carbons are commonly used in the treatment of waste water, namely as decontaminating agent of phenolic compounds. This work deals with the preparation of an activated carbon from an abundant local variety of date stones know Ghars. This natural product is largely exploited as a principal nutriment for animals alimentation. Two steps of the activation process are involved in this study, first, a physical treatment by carbon dioxide and second, the characterization of the resulting activated carbon followed by modelization procedure using 4-chlorophenol as test substrate. On the basis of the BET results, we have obtained a specific surface of $604 \, m^2/g$ and microspores volumes of $0.29 \, cm^3 \, g^{-1}$. In addition, the adsorption capacity was about 28.57 mg/g according to Langmuir model. The physical activation method utilized in this task was achieved by using carbon dioxide. Textural characteristics of the resulting activated carbon were carried out by nitrogen adsorption at 77 K along with application of BET equation for determination of surface area. Total volume of pores was determined by αs method. External surface area, micropore area and micropore volume were determined by t-plot method. The comparison of raw material, pyrolysât vis-à-vis the activated carbon was based on the elemental analysis of the principal elements. The adsorption capacity of the different prepared activated carbons was tested by using 4-chlorophenol as substrate.

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1. Introduction

Activated carbon is perhaps one of the most widely used adsorbents. Over the last few decades, an adsorption system involving this material has gained importance in purification and separation processes on an industrial scale. It is now considered as one of the best available technologies in removing both organic and inorganic trace contaminants. Its use can be broken down into discrete areas such as effluent treatment, potable water treatment, solvent recovery, air treatment, decolorizing, metal ore processing, and many more general domestic applications. This explains the increasing market trend for the use of activated carbons [1].

The methods of activation commonly employed can broadly be divided into two main types: physical and chemical activation. The first one involves primary carbonization (below 700 °C) followed by controlled gasification under the action of oxidizing gases at high temperature (up to 1100 °C) [2].

The chars produced by the carbonization process react with oxidizing gases such as steam (H_2O), carbon dioxide (CO_2), air or any mixture of these gases, resulting in the evolution of carbon oxides from the carbon surface. It is a complex heterogeneous process encompassing the transport of gas agents to the sample surface, their diffusion into the pores, sorption on the pore surface, reaction with carbon component, desorption of the reaction products and diffusion of these products to the atmosphere [3].

However, in the second one the precursor is mixed with a chemical restricting the formation of tars (e.g. $ZnCl_2$, H_3PO_4, etc.), after

Nomenclature

P/P°	relative pressure
S_{BET}	the specific surface area calculated via BET equation $(\mathrm{m^2/g})$
S_{ext}	external surface area $(\mathrm{m^2/g})$
S_{micro}	micropore area $(\mathrm{m^2/g})$
V_T	total volume of pore $(\mathrm{cm^3\,g^{-1}})$
V_{micro}	micropore volume $(\mathrm{cm^3\,g^{-1}})$
D_p	pore diameter $(\mathrm{nm}) = 4V_T/S_{BET}$
b	Langmuir equilibrium parameter (L/mg)
q_m	maximum adsorption capacity (mg/g)
q_e	adsorption capacity at equilibrium (mg/g)

kneading carbonized and washed to produce the final activated carbon. The chemical incorporated into the interior of the precursor particles reacts with the thermal decomposition products reducing the evolution of volatiles and inhibits the shrinkage of the particles. In this way, the conversion of the precursor to carbon is high, and once the chemical is eliminated after the heat treatment, a large internal porosity is formed [4].

Activated carbons can be prepared from many organic materials having high carbon content like wood [5,6], coal [7], lignite [8] and coconut shells [9–11]. In the recent years, many other agricultural by-products have been used as sources for activated carbons production such as cherry stones [12,13], olive stones [14–19], oil palm stones [20–22], apricot stones [23,24], almond shells [25], sugar cane bagasse [26,27], walnut shells [14], pecan shells [28–30], cotton stalks [31] and date stones [32–41].

Indeed, the use of these by-products allows their revalorization in a new finished product usable in industry. The study of the activated carbons starting from the vegetation wastes comes as result to the increasing demand for adsorbent materials. In this paper, we have paid attention to a particular date stones variety know Ghars.

World production of dates was approximately 8.6 million tons in 2004. The major producers in the world are: Egypt, Iran, Saudi Arabia, United Arab Emirates, Pakistan, Algeria and other mediterranean countries. Algeria produces 450,000 t/year of dates [42]. Date stones represent about 10% of the date weight. The chemical composition of the date stones consists of crude fiber and carbohydrates of hemicellulose (23%), lignin (15%), cellulose (57%) and ash (5%). Date stones are removed from dates during manufacturing and considered harmful to the environment. It has been shown by many researchers [43,44,29] that lignocellulosic agricultural wastes are good precursors for the production of activated carbon. Therefore, the possibility of using date stones as a source for activated carbon production should be investigated.

2. Experimental procedures

2.1. Samples preparation

The stones of dates used in this study are hard seeds of variable sizes. After separation from the fruit, they were washed and dried in the oven at 120 °C over 24 h. The resulting product is then crushed and preserved in hermetically closed bottles. The precursor is sieved into two fractions where $d_1 > 1$ mm and $d_2 < 250\,\mu$m.

2.2. Elemental analysis

The elemental analysis of C, H, N and O were carried out at the SCA-CNRS laboratory using micro analytic devices ensuring a precision of $\pm 0.3\%$ for the major components (>10%). A LECO analyzer

(model SC144) was used for S determination. The major results are assembled in Table 1.

2.3. Pyrolysis and activation

A vertical furnace (Ref. BGVA12-300B from CARBOLITE, UK) is connected to the inlet and outlet devices allowing an upward gaseous flow through the sample. About 75 g of crushed date stones are introduced in a cylindrical quartz cell (40 mm diameter) including a frit disc at half-height. The pyrolysis is carried out in the vertical furnace in the following range of temperature 700–900 °C with a rate of 15 °C/min and under a nitrogen flow of 250 mL/min. We have obtained, in these under these conditions two different sizes. The activation treatment of the pyrolyzed material was carried at 900 °C in the vertical furnace with the same quartz cell. The CO_2 flow rate used was 250 mL/min.

2.4. Porosity

Adsorption isotherms were obtained from the adsorption of nitrogen at 77 K on to the precursors using the ASAP 2010 (Micromeritics). The BET surface area (S_{BET}) was calculated according to Brunauer–Emmett–Teller (BET) equation [45]. The micro porous surface (S_{micro}), the external surface (S_{ext}) and the micropore volume (V_{mic}) were evaluated by the t-plot method from the adsorption isotherms data within the 0.1–0.3 relative pressure range (P/P°). The total pore volume was calculated by the (αs) method and the Dubinin–Radushkevich equation [46].

3. Results and discussion

3.1. Pyrolyzed materials

3.1.1. Yields

The particle size is a parameter which shows a large effect upon the pyrolysis yield. Indeed, yields around 24% are obtained for the smaller class ($d < 250\,\mu$m) while larger particles ($d > 1$ mm) give 33%. This observation is unexpected and contrary to Demirbas [47] ones for the pyrolysis yield of other agricultural residues (olive husk, corncob and tea waste).

3.1.2. Elemental analysis

The results of thermal treatment of the different samples, as illustrated in Table 2, leads to an increase in carbon percentage contrary to hydrogen and oxygen contents. In fact, the stage of pyrolysis makes possible to obtain of a carbonaceous product by the volatilization of hydrogen, oxygen, nitrogen and sulphide traces. It was postulated that tar, which is defined as the whole of the organic compounds having a molecular weight higher than that of the benzene [48], represent the main resulting product during this process. Tar is a mixture composed of condensable hydrocarbons including 1–5 aromatic nuclei, oxygenated hydrocarbons and complex aromatic hydrocarbons. In the process of pyrolysis the elimination of hydrogen and oxygen occurs in the form of CO, CO_2 and H_2O. The release of monoxide and carbon dioxide is generally observed between 200 and 300 °C. The cellulose is degraded between 240 °C and 360 °C [49]. At 300 and 400 °C, there should be the production of hydrocarbons, between 400 and 500 °C, a release of a large quantity of gas hydrocarbons and thick tar. From 500 to 700 °C, the production of gas refers mainly to hydrogen, carbon monoxide and hydrocarbons. From 700 with 1000 °C, the major remaining product is carbon residue. On the basis of that, we can draw the following notes:

Table 1
Elemental analysis of the precursors.

Sample reference	Element (%)							References
	C	H	N	O	S	C/H	O/C	
RDS$_1$	45.03	7.22	0.56	45.59	<0.10	0.52	101.2	This work
RDS$_2$	51.65	6.51	0.59	40.73	0.14	0.66	78.9	This work
Date pits	45.90	6.43	0.66	47.62	0.38	0.59	103.7	[41]

Table 2
Yield and elemental analysis of the pyrolyzed materials.

Sample reference	Yield (%)	Element (%)						
		C	H	N	O	S	O/C	C/H
PDS$_1$700	24.64	86.94	1.42	1.73	5.78	<0.20	6.64	5.10
PDS$_1$800	24.13	90.59	1.08	2.42	5.17	<0.20	5.71	6.99
PDS$_1$900	24.49	92.70	0.95	2.08	4.24	<0.20	4.57	8.13
PDS$_2$700	33.22	86.00	1.65	2.01	5.18	<0.20	6.02	4.34

Table 3
Burn-off and elemental analysis of the activated samples.

Sample reference	Burn-off (%)	Element (%)						
		C	H	N	O	S	O/C	C/H
ADS$_1$900/700	24.1	86.96	0.93	2.59	7.69	<0.20	8.84	7.79
ADS$_1$900/800	18	89.48	0.95	2.44	6.98	<0.20	7.80	7.85
ADS$_1$900/900	15.7	89.18	0.90	1.78	6.81	<0.20	7.63	8.25
ADS$_2$900/700	33	84.53	1.16	2.23	7.67	<0.20	9.07	6.07

- An increase of the (C/H) ratio with the pyrolysis temperature was observed, indicating a higher degree of aromatization and accordingly a polymerization process might take place.
- A slight effect of the particle size on the elemental analysis.

3.2. Burn-off and elemental analysis of the activated sample

In all activated carbons, the contents of carbon were increased whereas the contents of hydrogen and oxygen are decreased (Table 3). This is due to the release of volatiles during pyrolysis that result in the elimination of the non-carbon species and enrichment of carbon. It is clear that the carbon content of activated carbon is significantly higher after activation, and the oxygen and hydrogen are lower. Another factor leads to the formation of microspores during activation when temperature exceeds 700 °C. The changes in the elemental content agree with the concentration of oxygen surface functional groups. In contrast, the annealed sample possesses the lowest oxygen content. This is expected, since at elevated temperature most of the acidic oxygen-containing functional groups are unstable and are subsequently removed. The O/C %, representing a normalized property of each coal shown, is employed instead of the oxygen content in following discussion of the oxygen impact throughout this report. One notices that O/C % ration is very important for the samples raw, then decreased for the pyrolyzed samples (that is with the volatile matters), on the other hand one will have an increase with the temperature of activation. The classification of the supports with respect to O/C ration is the same for bulk phase and for surface.

3.3. Textural properties of the activated carbons

The analysis based on physical adsorption isotherms is a technique widely used in determining the porous texture of a given solid [50]. In the present study, CO_2 was selected as the activation gas; CO_2 is clean and easy to handle. Moreover, CO_2 has been a preferred choice as the activation gas on the laboratory scale; it facilitates control of the activation process due to the slow reaction rate at temperatures around 800 °C [51] as it is illustrated by the following postulated reaction mechanism equation:

$$C + CO_2 \rightarrow 2CO \quad \Delta H_{298\,K} = 159\,kJ/mol \tag{1}$$

During CO_2 activation, the particle size might influence its diffusion into the interior as well as the release of the resulting gaseous products. Normally the larger the particle, the more difficult it would be for the gas to penetrate into the sample and also for the gaseous products to emit to the ambient. These might retard the reaction between the sample and CO_2 gas, thereby limiting further pore development in the sample.

Table 4 shows that the ratio of the microporous surface to the total surface area (S_{micro}/S_{BET}) varies from 83% to 87% for date stone (index1) and 79% for date stone (index2), the ratio of the microporous volume to the total pore volume (V_{micro}/V_T) varies from 83% to 85% and 76% for date stone (index1) and date stone (index2) respectively. Therefore, the produced pores during activation of pore size $\sim$ 2 nm, as listed in Table 4, are predominantly nearest to the micropore dimensions and exceed the half of total pores (V_{micro}/V_T). The values of V_{micro}/V_T again indicate the predominance of micropore volumes. As it can be seen in Table 4 a progressive increase in the external surface area (S_{ext}) takes place during the initial stages of the activation process. External surface corresponds to the slope of the linear part of the graph of comparison. This part is generally in the: 0.2–0.3 < $P/P°$ < 0.7–0.8 range.

The specific surface area S_{BET} (m^2/g) as well as V_T (cm^3 g^{-1}) and V_{micro} (cm^3 g^{-1}) increases with the pyrolysis temperature under the same conditions of activation then decreases. This is due to the partial closing of microporosity (micro reduction of V_{micro} from 0.26 to 0.23 cm^3 g^{-1}). Concerning the dimension of the particles; the activated carbon having gross particles will be adsorbed better than fine particles ones.

The sorption isotherms (Figs. 1 and 2) of activated carbons are of type I according to the IUPAC classification [52]. This shape is characteristic of the presence of microporous structure with a rather narrow pore size distribution.

Table 4
Reports the textural properties of the samples studied obtained from N_2 adsorption isotherms at 77 K.

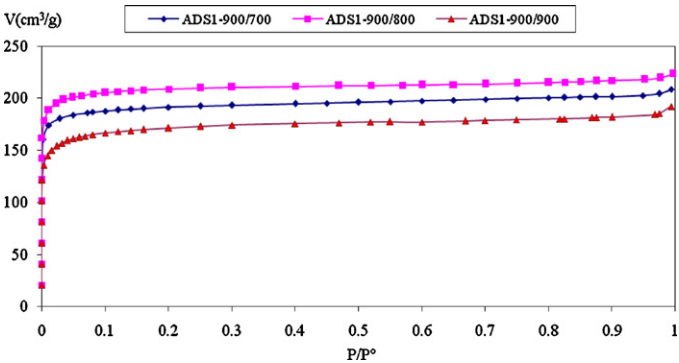| Samples activated carbon	Characteristics of activated carbon									
	Burn-off (%)	The specific surface area (S_{BET}) (m²/g)		t-Plot method			αs method	S_{micro}/S_{BET} %	V_{micro}/V_T %	D_p (nm)
		Langmuir	BET	S_{ext} (m²/g)	S_{micro} (m²/g)	V_{micro} (cm³ g⁻¹)	V_T (cm³ g⁻¹)			
ADS$_1$900/700	24.1	854	554	76	478	0.26	0.32	86	83	2.28
ADS$_1$900/800	18.0	928	604	77	527	0.29	0.34	87	85	2.25
ADS$_1$900/900	15.7	787	511	83	428	0.23	0.28	83	83	2.21
ADS$_2$900/700	33.0	775	502	105	397	0.21	0.29	79	76	2.28

Fig. 1. Adsorption isotherm of N_2 on activated carbon (effect of temperature on pyrolysis).
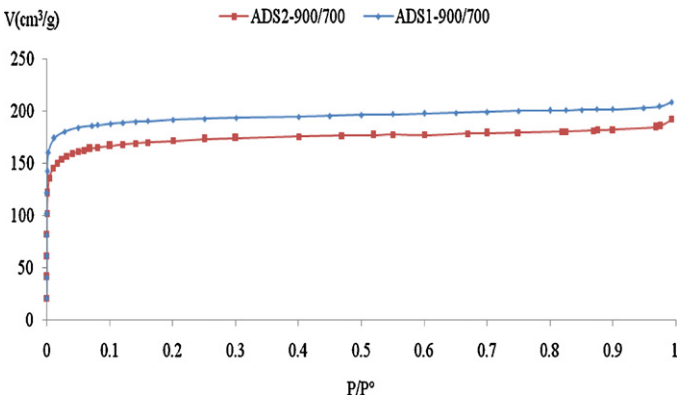

Fig. 2. Adsorption isotherm of N_2 on activated carbon (effect of the particle size).

3.4. Adsorption capacity in aqueous solutions

The presence of chlorophenols in the aquatic environment has been a big deal to scientists due to their increased discharge, toxic nature, and other adverse effects on receiving waters. Even a very low concentration of chlorophenols in water is very toxic to aquatic life. The main sources of chlorophenols in water are the effluents of processing industries. Due to the fact that chlorophenols poisoning in human causes severe damage to the kidney, liver, and brain causes sickness or death. The present work was concerned the removing of 4-chlorophenol using the prepared activated carbon as adsorbent.

The adsorption of 4-chlorophenol is carried out in discontinuous reactor in a series of small glass bottles of 30 mL, 0.1 g of the adsorbent is added to 25 mL of micropolluant at different concentrations. These closed bottles are placed on a table of agitation (Carrousel model) with a controlled horizontal oscillation between 180 and 200 blows per minute (cps min^{-1}) during a time of average contact of 72 h to the end of which balance between the various phases is supposed already reached. Thereafter, the contents of the bottle are filtered by plastic filters of 0.2 μm and the filtrates are analyzed by UV-VIS (Model JASCO UV-970/975) with the maximum wavelength (= 282 nm. The isotherms of adsorption are carried out at ambient temperature (25 ± 0.2 °C) and the duration of agitation is the same one for all the bottles. The pH of the solution is between 6 and 7.

The equilibrium adsorption capacities (q_e) at different solute concentrations were determined according to mass balance on adsorbate:

$$q_e = \frac{(C_o - C_e)}{m} V \qquad (2)$$

Table 5
Parameters of the Langmuir isotherms for the adsorption of 4-chlorophenol on the activated carbon.

Sample	Pyrolysis conditions	Activation conditions	$S_{(BET)}$ (m^2/g)	K_L (L/mg)	q_{max} (mg/g)	R^2
ADS1-900/700	700 °C, 250 mL/min N_2, 15 °C/min, 2 h	900 °C, 250 mL/min CO_2, 15 °C/min, 2 h	554	0.03	27.78	0.999
ADS1-900/700	800 °C, 250 mL/min N_2, 15 °C/min, 2 h	900 °C, 250 mL/min CO_2, 15 °C/min, 2 h	604	0.24	28.57	0.999
ADS1-900/700	900 °C, 250 mL/min N_2, 15 °C/min, 2 h	900 °C, 250 mL/min CO_2, 15 °C/min, 2 h	511	0.18	23.80	0.999
ADS2-900/700	700 °C, 250 mL/min N_2, 15 °C/min, 2 h	900 °C, 250 mL/min CO_2, 15 °C/min, 2 h	502	0.12	23.25	0.999
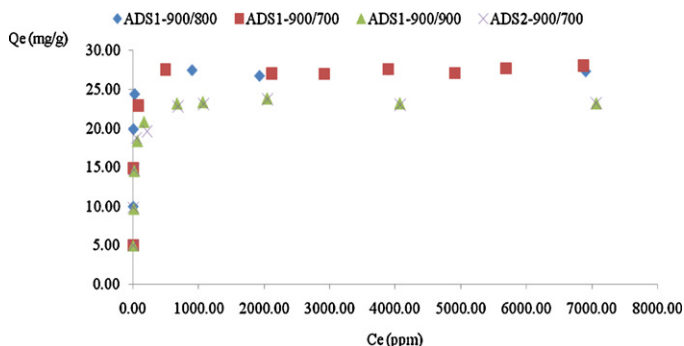
Fig. 3. Adsorption isotherms of 4-chlorophenol onto activated carbon.

where C_o is the initial 4-chlorophenol concentration, C_e the equilibrium 4-chlorophenol concentration ($mg\,L^{-1}$), m the amount of activated carbon (g) and V solution volume (L).

The Langmuir [53] model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Our results of 4-chlorophenol adsorption on the prepared activated carbons showed that Langmuir adsorption isotherm was obeyed (Fig. 3) which may be expressed by the linear equation [53]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \qquad (3)$$

where q_e is the amount of 4-chlorophenol adsorbed onto activated carbon at equilibrium (mg/g), q_{max} is the theoretical monolayer capacity (mg/g), K_L is the Langmuir equilibrium constant related to the affinity of binding sites and energy of adsorption (L/mg) and C_e is the equilibrium solution concentration ($mg\,L^{-1}$). The Langmuir equation is considered suitable for homogeneous surfaces [54]. Parameters of Langmuir isotherm are listed in Table 5.

It appears from Fig. 3 and Table 5 that

1. The adsorption isotherms of 4-chlorophenol, according to Giles et al. group classification, belongs to the L curve pattern. Otherwise, there is no strong competition between solvent and the adsorbate in occupying the adsorbent surface sites [55].
2. The adsorption of 4-chlorophenol on the different activated carbons coincides with Langmuir model where the coefficients of correlation were considerably important ($R^2 \geq 0.999$).

4. Conclusions

In this study we have succeeded to valorize a local byproduct of date stones (Ghars variety) via its implication as an adsorbent of a potent phenolic derivative compound 4-chlorophénol. The resulting product has had a BET surface areas ranging from 502 to 604 m^2/g, and a ratios of micropore volumes to the total pore volume ranging from 0.76 to 0.85. The obtained adsorption capacity lies between 23.25 and 28.57 mg/g. On the basis of this non-exhaustive study, it could be noted that this variety of stone dates presents an interesting adsorptive proprieties. Accordingly, this material might be used as support in heterogeneous catalysis. Optimization of these results will be the platform of our future investigations.

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