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REMOVAL OF ORGANIC POLLUTANTS FROM WASTEWATER BY ACTIVATED CARBON PREPARED FROM DATES STONES OF SOUTHERN ALGERIA

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ABSTRACT

The aim of this work is to prepare activated carbon from date seeds to treat wastewater. The study of the characteristics of activated carbon from El-Oued dates gave the following results: surface area (125.86m^2/g), pore volume (0.039cc/g), pore size (16.25µm), microspores surface area (92.28 m^2/g), the external surface (33.57 m^2/g), methylene blue index (13.6 mg/g), iodine number (735.2 mg/g) and amount of functional groups (4.10^{-2} mol/g).

The best conditions for the removal of organic pollutants are: contact time (5 min), stirring speed between 200 and 300 rpm and a pH below 5 or above 8.

The removal of organic pollutants in wastewater from El-Oued region prepared by the charcoal has led to very significant abatement rate: COD (86.9%) and BOD_5 (87.55%).

Keywords: Date palm, Activated carbon, Wastewater, El-Oued, Purification

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1. INTRODUCTION

The valuation of various wastes and agricultural by-products has achieved more or less effective activated carbon in various applications, and various precursors were used: apricot

kernels [1], agricultural waste biomass [2], coconut waste [3], by-products of cereals [4], olive pits [5] and kernels jujube [6] .

The objective of this work is to develop a by-product of the date palm, whose heritage in Algeria exceeds 18 million date palms with 800 varieties and an annual output that exceeds 780.000 tonnes [7].

The unused date stones which are produced with huge amount every year were chosen to produce the active carbon which is used in wastewater treatment.

Several studies used a charcoal prepared from the date stones such as: removal of cadmium [8], removal of volatile organic compounds [1].

In the first stage of this work, we prepared the charcoal from the date seeds, then determined its characterization. In a second step, the activated carbon is used for removing organic pollutants in wastewater from the same region for the perpous of determining the best conditions for adsorption.

2. RESULTS AND DISCUSSION

2.1. Characterization of the prepared activated carbon

2.1.1. Adsorption and desorption isotherms of nitrogen at 77°K on carbon

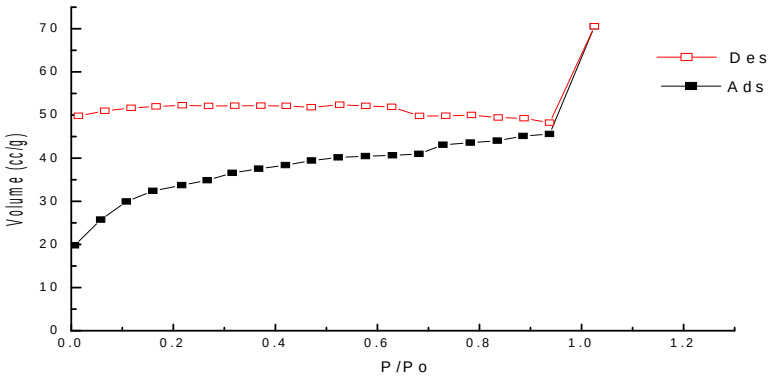

Fig.1 Adsorption and desorption isotherms of nitrogen at 77 °K on carbon

The adsorption isotherm obtained is shown in Fig.1 determines the existence of a horizontal, indicating a saturation of the adsorbent in spite of the increase in pressure. This is an isothermal of the first type; one can say that the surface of our adsorbent is essentially constituted by micropores.

2.1.2. Surface area, external surface area, micropore area, micropore volume and correlation coefficient

The results of the method are summarized in Table 1.

Table1 Results of BET

Surface area (m^2/g)	125.863
Outer surface (m^2/g)	33.578
Microporous area (m^2/g)	92.285
Micropore volume (cc/g)	0.03
Correlation coefficient	0.949

2.1.3. Result of the electron microscope SEM

The pictures of the morphology of the prepared activated carbon obtained by scanning electron microscopy expansions 800 and 2400 are presented in Fig 2 and Fig 3.

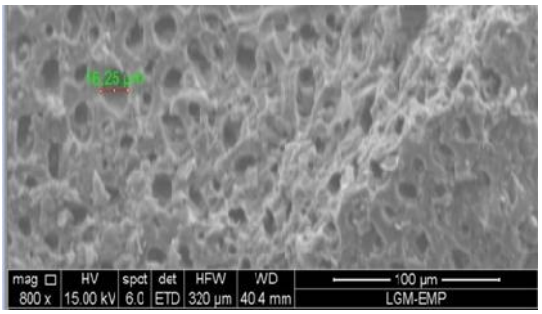

Fig.2. SEM micrographs for AC particles $_x$ 1200

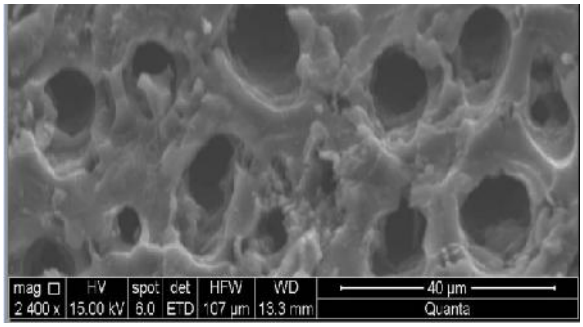

Fig.3. SEM micrographs for AC particles $_x$2400

At the magnification 800 times, a sufficiently developed porosity is observed over the entire sample surface.The pore distribution is very irregular.The expansion in 2400 clearly shows both the porosity very developed on the surface of the prepared activated carbon.

2.1.4. Result analysis by IR

The chemical structure and the functional groups of activated carbon were determined from the Infrared spectrum Transformed Fourier presented in Fig.4.

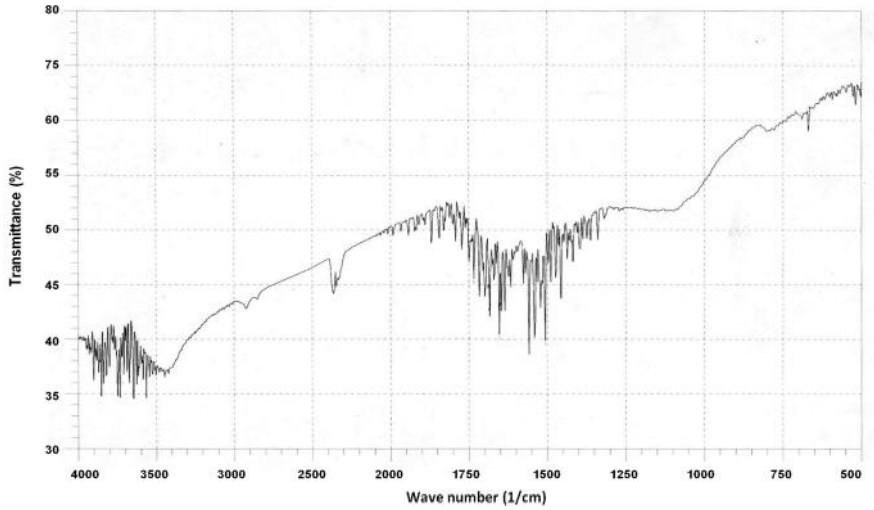

Fig.4. FTIR spectrum of the activated carbon

Table 2. Functional groups in FTIR spectrum

Wave Number (cm^{-1})	Bonds
3400	N-H amine and imine (valence)
2900	C–H vibrations in methyl and methylene groups (valence)
2350	C= N nitriles (valence)
1570	N=O (valence)
1700	C= O aldehyde and acetone groups (valence)(
1091.6	C-C groups (valence)
1450	C= C Aromatic (valence)
1320	C-O alcools and ether groups (valence)

There are a lack sulfide groups and phosphorus and the presence different groups of oxygens in particular carbonyl, alcohol and aromatic groups as well as amine groups.

2.1.5. Methylene blue index and iodine value

Methylene blue is known by the evaluation of activated carbon's ability to adsorb large molecules, while the iodine value characterizes the performance activated carbon for the removal of low molecular weight compounds. Obtain the concentration of methylene blue from the graph in Fig 5.

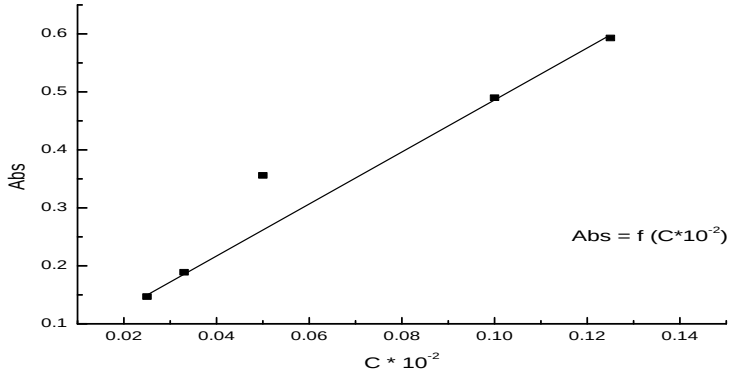

Fig.5. Witness curve to measure the concentration

The methylene blue index is equal to 13.6 mg/g, whereas the iodine number is 735.2 mg/g. The activated carbon that we prepared is thus better suited to the adsorption of low molecular weight molecules. This confirms that the coal studied primarily has a microporous structure. These results confirm those obtained by the scanning electron microscope SEM.

2.2. Adsorption of the organic pollutants

2.2.1. Influence of contact time

The experiments were performed on the wastewater treatment in El-Oued city .

The study of the influence of contact time is carried out under the following experimental conditions: pH = 7.64, V = 20 ml, COD (raw waste water): 630 mg/l, BOD_5 (raw waste water): 400 mg/l, active carbon mass: 0.5 g.

The evolution of the COD and BOD_5 are presented in Fig.6 and Fig 7 respectively.

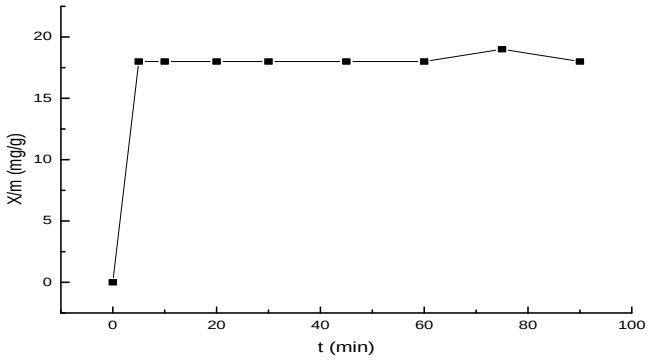

Fig.6. Amount absorbed depending on the contact time for COD

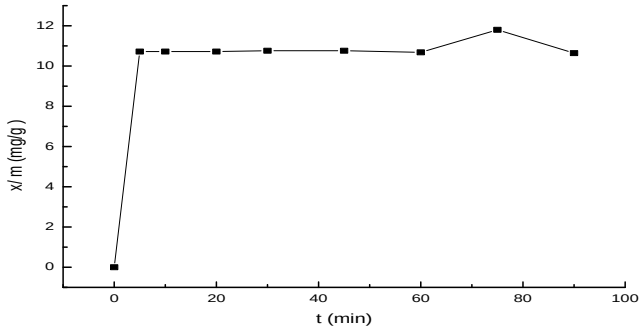

Fig.7. Amount absorbed depending on the contact time for BOD_5.

Note that in the first 5 minutes, there is the elimination of a considerable amount of organic pollution that reaches adsorbed amount of 18 mg/g for COD and 10.5 mg/g for BOD5.

This step depends on transfer of the adsorbed material from the liquid phase on the surface of activated carbon. After the first five minutes the adsorbed amount remains constant, there is a balance between adsorption and desorption. The number of available active sites on the surface of the adsorbent material is higher than the reaction at sites still available later [10].The second part is slower. This phase corresponds to the establishment of equilibrium between the adsorption speeds and desorption. The optimum time for adsorption is five minute

2.2.2. Influence of pH

The study of the influence of pH is carried out under the following experimental conditions: V = 20 mL, COD (raw waste water): 988.4 mg/L BOD5 (raw waste water): *400* mg/L, massactive carbon: 0.5 g.Fig. *8* reflects changes in pH for COD: 4; 5; 6; 7; 8; 9.Fig. 9 reflects changes in BOD5 for the same pH values.

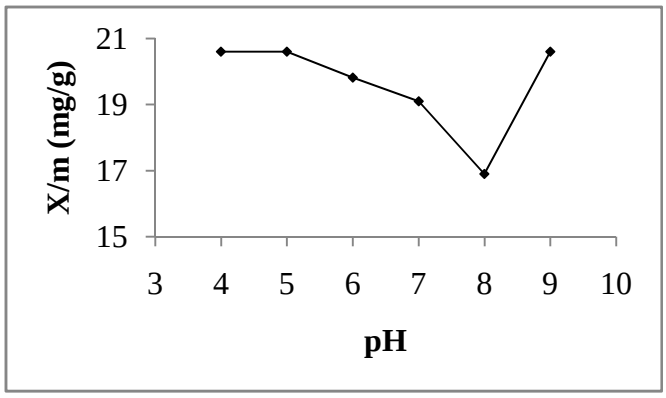

Fig. 8. Curve of the amount adsorbed versus pH

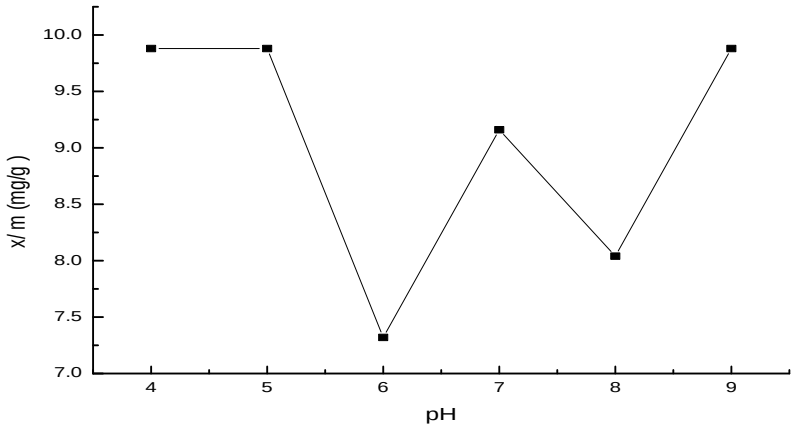

Fig.9. Curve of the amount adsorbed versus pH

According to the curve there is a relationship between pH and adsorption of organic pollutants on the surface of activated carbon .The amount adsorbed keeps roughly the same value for pH 4.5 and 9 . The instability is observed for pH between 5-9 where adsorbed amount decreases and then increases to pH = 9.

This could be explained by the fact that the change in pH affects the change of the ionic charge of the adsorbed material which changes the adsorbate-adsorbent attraction force. Next the pH of new active sites may appear or disappear.

2.2.3. Influence of Stirring speed

The study of the influence the rate of stirring is carried out under the following experimental conditions: V = 20 mL, COD (raw waste water): 988.4 mg/l, BOD_5 (raw waste water): 400 mg/l, activated carbon mass: 0.5 g.

Fig10 reflects changes in COD for stirring speeds of 200, 400, 600, and 800 r/min.

Fig11reflects changes in BOD5 for the same values of stirring speeds.

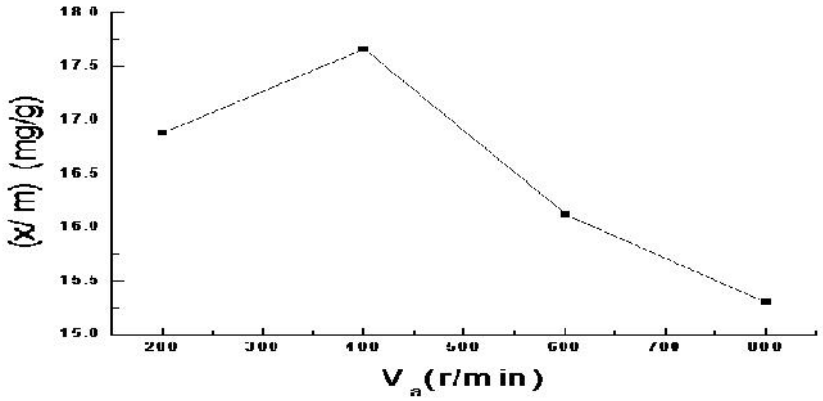

Fig.10. The curve of the amount adsorbed depending on stirring speed (COD)

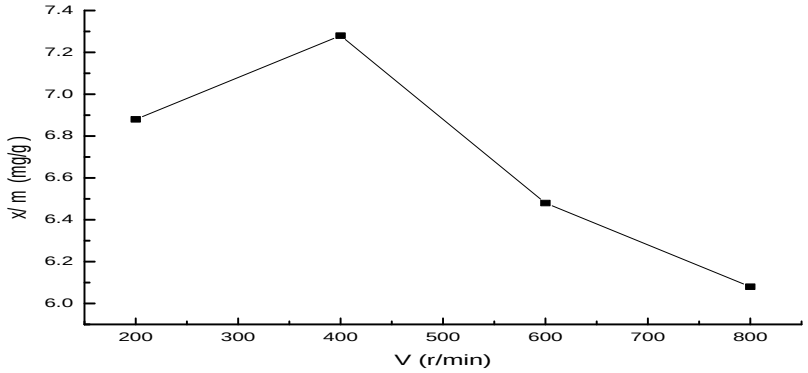

Fig.11. The curve of the amount adsorbed depending on stirring speed (BOD_5)

The stirring speed is changed between 200-800 rpm. The maximum value is obtained at a speed of 400 rpm.The maximum amount explains the saturation of the surface of active carbon. After 400rpm, pollutants are desorped.We can say that the great stirring speed leads to failure of the bond-absorbing adsorbent which leads to the disappearance of the adsorbed material on the surface of activated carbon.

Treatment result of the prepared activated carbon by fixing the pH at 7.8 and following the removal rate of organic pollutants through the COD and BOD_5.

Table 3. Application Results of activated carbon wastewater treatment plant in the city of El-Oued

Pollutant	Raw water	Treated water	Yield %
COD (mg/l)	611.10	80	86.90
BOD_5 (mg/l)	269.16	33.5	87.55

The removal of organic pollutants is a very significant way in terms of COD and BOD_5, the high adsorption capacity is definitely prepared microporosity of activated carbon. These results confirm the results of the study of active coal properties.

3. EXPERIMENTAL

3.1. Preparation of activated carbon

The dates of the variety Deglet Nour is collected. Dates cores are extensively washed with tap water, then with distilled water until free of all impurities.

The date seeds are dried in an oven for 24 hours at a temperature of 100 °C.The seeds are then ground and sieved to obtain only the particles whose diameter is between 0.5 and 2 mm.Then followed by the chemical activation of selected grains before carbonization [9].

The activation is carried out with concentrated H_3PO_4 in a volume ratio acid-water 1/1.

After chemical activation the sample is placed for 1 hour in an muffle oven at a temperature of 100 °C. The sample is then dried in an oven for 24 hours at a temperature of 100 °C (the start time contact is established from the time where the temperature reaches 100 °C). To protect the sample from the air, it is transferred from the oven directly to the furnace where it is held for one hour at a temperature of 300 °C.

The sample is mixed without being in contact with a large amount of oxygen.

After closing the furnace, the temperature was raised to 350°C for a quarter of an hour.

We continued according to the preceding steps to a temperature of 450 °C with mixing each quarter of an hour with little oxygen.The oven is closed to ambient temperature. After carbonization it is washed with10% HCl to remove impurities. Finaly it is washed with distilled water until neutral. Washing with distilled water is done for at least three days**.**

3.2. Characterization of the prepared activated carbon

3.2.1. Surface area, outer surface, microporous surface, micropore volume and correlation coefficient

The surface area is evaluated by the equation of Brunauer-Emmett-Teller (BET).

The microporous surface, micropore volume, coefficient Corrélation are determined from the t-plot method of DeBo.The outer surface is derived from the formula $S_{ext} = S_{BET} - S_{micro}$.

3.2.2. Scanning electron microscopy (SEM)

A scanning electron microscope (Quanta 60 MBL / EMP) was used for the investigation of the morphology of the surface of the prepared activated carbon.

3.2.3. Analysis by Infrared (FTIR)

Infrared spectrometry with Fourier transform is performed using an infrared spectrophotometer over the range of wave longuers from 400 to 4000 cm^{-1}.

3.2.4 Surface Functional group

Surface Functional Groups are determined by the Bohame method.

In an Erlenmeyer flask is placed 0.5 g activated charcoal with 50 ml of a solution of 0.1 mol/l NaOH under stirring for 24 hours. After filtration the filtrate is titrated with an HCl solution of 0.1 M. It is necessary that the medium does not contain carbon dioxide. The value must be shown in mmol.

3.2.5 Methylene blue index

The concentration measurement is carried out using a UV-visible spectrophotometer (OPTIMA, SP-3000 plus) at 660 nm, placed 0.5 g activated charcoal in 100 ml of methylene blue solution concentrated to 1000 mg/l, under continuous stirring for 24 hours. After filtration, measures the concentration of the filtrate.

3.2.6 Iodine index

Put 0.5 g of activated charcoal in an Erlenmeyer flask. Add 10 ml of sulfuric acid at 5% then stir until the charcoal is moistened. Heat the mixture until boiling. Let is cooled for 30 minutes . Add 100 ml of iodine solution 0.1mol/l with stirring for 30 minutes then filter it. Neutralize 50 ml of the filtrate by 0.1 M thiosulfate solution.

3.3. Adsorption of the organic pollutants

The wastewater samples are taken at the entrance to the sewage treatment in El-Oued city, using an automatic sampler ASP Station 2000, according to the NF EN 25667 (ISO 5667). Samples are transported to the laboratory for analysis in polyethylene containers at a temperature of 4 °C. 20 ml of wastewater is contacted with 0.5 g of the activated carbon. The COD and BOD_5 are determined before and after the treatment.

COD was determined according to standard NF T 90-101, using a spectrophotometer WTW Spectral Photo Lab.BOD_5 was determined according to the NF T 90-103 with a measuring BOD WTW OxiTop.We studied the influence of contact time, pH, the stirring speed and the concentration.

4. CONCLUSION

This work allowed us to value date stones, a waste of date palm in charcoal.The activated carbon that we have obtained has excellent textural properties (high porosity and large surface area): surface area 125.86 m^2/g, pore size 0.0039 cc/g, pore width 16.25 microns, external surface area 33.37 m^2/g, methylene blue index 13.6 g, iodine number 735.2 mg/g, amount of functional groups 1.4 x 10^{-2} mol/g.

The best conditions for the removal of organic pollutants are: a contact time of 5 minutes, a stirring rate between 200 and 300 rpm and a pH is less than 5 or greater than 8.The removal of organic pollutants in wastewater from El Oued region prepared by the charcoal has led to very significant abatement rate: COD (86.9%), BOD_5(87.55%).

5. ACKNOWLEDGEMENT

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