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## Elimination Of Phosphorus By Activated Carbon Prepared From Algerian Dates Stones.

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### ABSTRACT

The current work has as its goal the preparation of activated carbon from the stones of dates from southern Algeria (El-Oued province) using a simple pyrolysis proceeded by chemical impregnation in sulphuric acid. For the preparation of the carbon we choose the diameter of the pellets (0.5-1)mm, activation by acid and water (1:1), carbonization at 450°C. The prepared carbon has the following characteristics: specific surface 125.86 m<sup>2</sup>/g, methylene blue number 40, CCE = 0.3meq.g/l, IR and micrographics SEM. The activated carbon thus obtained is used at the water purification in wastewater treatment plant (WWTP) at Kouinine, El-Oued province, to totally eliminate phosphorus. We analyzed the water at the WWTP before the purification procedure. In this study we have looked at the effect of the following parameters on the adsorption of carbon: the pH, the contact time ( $T_c$ ) and the agitation speed ( $V_a$ ). The best conditions for phosphorus adsorption are: pH=4 or pH >5,  $T_c$  = 60 min and  $V_a$  = 900 rotations per minute.

**Keywords:** Date stones, activated carbon, pyrolysis, phosphate pollutants.

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## INTRODUCTION

Interest has been generated worldwide concerning the protection of the environment from solid waste arising from the different human activities and transformations. Researchers have been trying to find techniques to recover this waste. Producing activated carbon from vegetable waste is interesting from the economic point of view because it is from simple transformative techniques that direct applications for these materials can be found. Activated carbon is an inexpensive material which can be obtained by carbonization and activation of an original material which already contains a significant amount of carbon and a small percentage of inorganic matter [1]. It can be produced in two ways: either by physical activation or chemical activation. Different studies have looked at the production and description of activated carbon produced from a variety of vegetable sources, such as coconut shells [2], almond shells [3], peach stones, rice hulls, apricot stones, cherry stones, olive stones, peanut hulls, palm shells, pistachio shells, coir pith, pecan shells, banana pith and sugarcane bagasse [4-14]. It is within this context that this work aims to highlight production of activated carbon from date stones. In fact the residue of dates used in several food and non-food fields. Previous studies have shown that date stones contain significant proportions of polyphenols and essential oil [15].

We were interested in the transformation of these by products into activated carbon by chemical means using sulphuric acid as a chemical activating agent [16]. In this study, stones from the Algerian date, known in the region under the popular name of "Ghars" grown in the El-Oued area, have been used for the production of activated carbon which has then been used with wastewater to eliminate phosphate pollutants. In order to choose the best ways to eliminate the phosphate pollutants, we examined the following parameters: the pH, contact time and agitation speed.

## MATERIAL AND METHODS

### Sampling and operation

Water sampling was carried out according to the standard AFNOR NF EN 25667 (ISO 5667). Samples were collected at the untreated stage of entry into the wastewater treatment plant at Kouinine (El-Oued) using a stipulated automatic sampler of the type ASP Station 2000, using a time interval of approximately every 10 minutes for a 24 hour period. For this a polyethylene flask 12 x 3 liter was used at a refrigerated temperature of 4°C. The samples were collected at the end of the day and mixed in order to obtain a single representative sample. Samples were taken to the laboratory in a cool box at 4°C and analyzed within 24 hours.

The following physicochemical parameters were measured: pH, temperature, turbidity, dissolved oxygen, COD, BOD<sub>5</sub>, TSS and nutrients.

The pH and temperature (T) were measured by a pH meter (EUTECH Instruments 510)

The dissolved oxygen was measured using an Oximeter (WTW with a 730 electrode).

The turbidity was measured by a Turbidimeter (WTW Turb 550 IR).

The biochemical oxygen demand after 5 days (BOD<sub>5</sub>) was determined using a gauge device WTW OxiTop), in an enclosure at 20°C according to the AFNOR 90105 standard. The chemical oxygen demand (COD), the total nitrogen (Nt) and the total phosphorus (Pt) in the untreated water was measured using a spectrophotometer (WTW PhotoLabo spectral). The amount of phosphorus was determined in both the untreated and treated water.

The test stock solutions were taken directly at the entrance to the plant.

The pH of the test solutions was adjusted with hydrochloric acid or sodium hydroxide.

## **Preparation of the activated carbon**

### **Collection and pretreatment of the raw material**

The date stones were food-processing waste collected from the industry in the province of El-Oued in Algeria. They were thoroughly washed in distilled water then dried in an oven (select-horn 2200) at 110°C for 24 hours. They were then crushed and sieved (AFNOR sieve) to hold back particles sized between 0.5 and 1mm. Chemical activation with sulphuric acid.

The retained particles were soaked in a solution of sulphuric acid with a concentration of 1:1. The soaking was done in an oven at a temperature of 105°C for 24 hours. The particles were kept in hermetically sealed flasks until the carbonization tests.

The carbonization was carried out at temperature of 450°C. The carbon thus obtained was cooled to ambient temperature in a desiccator. In order to remove possible residues from the carbonization process, the activated carbon was washed in a solution of hydrochloric acid 0.1M then rinsed several times in distilled water until the pH was constant [17]. The rinsed carbon was then dried at 105°C for at least 8 hours in an oven, then cooled in a desiccator and kept away from the air in hermetically sealed flasks until the characterization tests.

### **Characterization of the activated carbon obtained**

#### **Surface chemical analysis (Capacity of Cation Exchange, CCE)**

In studies on activated carbon Boehm's titration is widely used to determine the CCE of adsorbents [18]. A balanced quantity of adsorbent (0.5g) was placed in an Erlenmeyer flask. A volume of 20ml of NaOH 0.1M solution was added. In order to reach equilibrium, the suspension was agitated for 24 hours. After filtration, the residual NaOH concentration was determined by titration with a hydrochloric acid solution 0.1M using phenolphthalein as an indicator. The amount of NaOH consumed was converted to CCE and expressed in meq.g/l [19].

#### **Methylene blue (MB) adsorption**

The adsorption of Methylene blue was carried out by mixing 0.5g of activated carbon prepared with a solution of Methylene blue 100ml of 1000mg/l [20]. After agitation for 24 hours, the suspension was filtered and the concentration of residual MB was measured at 660 nm using a UV spectrophotometer (OPTIMA, SP-3000 plus). A linear relation previously established by Beer-Lambert was used to determine the concentration.

#### **Analysis of morphology**

In order to know the visible structure of the activated carbon, a scanning electron microscope (SEM) was used to visualize the sample's morphology. The pore structure and structural changes which resulted after the chemical activation could also be seen. In the current work, the raw material (date stones) and the activated carbon prepared have been analyzed by this technique using a Philips XL30 microscope.

#### **Infrared spectroscopy**

For the qualitative determination of the surface functions, we used an infrared spectrometer-Infrared Tensor 27 (Bruker) with a resolution of 4cm<sup>-1</sup>. The base line was made with a KBr pellets and measurements made on the powders.

#### **Measurement of the BET specific surface**

The specific surface of the prepared activated carbon was evaluated by adsorption of N<sub>2</sub> at 77°K, using Autosorb-Quantachrome instrument. The BET (Brunauer-Emmet-Teller) model was applied in order to adapt the isotherm of nitrogen adsorption and to evaluate the surface area (S<sub>BET</sub>) of the sorption agent [21].

### Adsorption experiments

The working solutions were taken at the entrance to the WWTP Kouinine. In the study batches of the adsorbent were placed in a beaker containing 20ml of wastewater with the desired concentration. The floating liquids were filtered and the phosphorus concentrations determined with a UV/VIS spectrophotometer of the type Option pop.

### Influence of contact time

The experiments were carried out with an agitation speed of 300 rotations per minute, and a pH=7.5. The volume of the solution to be treated was 20ml. The quantity of the adsorbent was fixed at 0.5g. The initial concentration of the wastewater was 11mg/l.

### Influence of pH

The pH was adjusted to the required value with sulphuric acid or sodium hydroxide. During the tests, the pH was adjusted between 4 and 9, the agitation speed was 300 rotations per minute, the quantity of adsorbent (0.5g) and the solution to be treated was 20ml.

### Influence of the agitation speed

The experiment was carried out on a hotplate (VELP scientific ) where we mixed 0.5g of adsorbent with a solution of wastewater (20ml) varying the agitation speed of the container between 200 and 900 rotations per minute in the following operating conditions:

The solution to be treated was 20ml, the quantity of adsorbent was fixed at 0.5g, the initial phosphorus concentration was 11mg/l.

## RESULTS AND DISCUSSION

The results of the analysis of water entering the Kouinine treatment plant are shown in Table 1.

Table 1: Physicochemical parameters

|                                                       |        |
|-------------------------------------------------------|--------|
| TSS (Total suspended solids, mg/l)                    | 278    |
| COD (Chemical oxygen demand, mg/l)                    | 611.1  |
| BOD <sub>5</sub> (Biochemical oxygen demand, mg/l)    | 269.16 |
| O <sub>2</sub> (Dissolved oxygen, mg/l)               | 0.925  |
| N-NH <sub>4</sub> (Ammoniums, mg/l)                   | 65.43  |
| N-NO <sub>3</sub> (Nitrates, mg/l)                    | 0.80   |
| N-NO <sub>2</sub> (Nitrites, mg/l)                    | 0.351  |
| Nt (Total nitrogen, mg/l)                             | 85.44  |
| Pt (Total phosphorus, mg/l)                           | 10.83  |
| PO <sub>4</sub> <sup>-3</sup> (Orthophosphates, mg/l) | 6.84   |
| Turbidity (ntu)                                       | 280.7  |
| Conductivity (mS)                                     | 5.23   |
| T (°C)                                                | 15     |
| pH                                                    | 7.64   |

The analysis of water from the town of El-Oued and collected at the entrance to the wastewater treatment plant show that all of the values for TSS, the COD, the BOD<sub>5</sub>, dissolved oxygen, ammonium, nitrates and nitrites are within the brackets of average values generally observed for urban wastewater [22], however a significant part of the nitrogen pollution corresponded to Kjeldahl nitrogen.

The same observation can be formulated concerning the physicochemical parameters.

**Characterization of the carbon obtained**

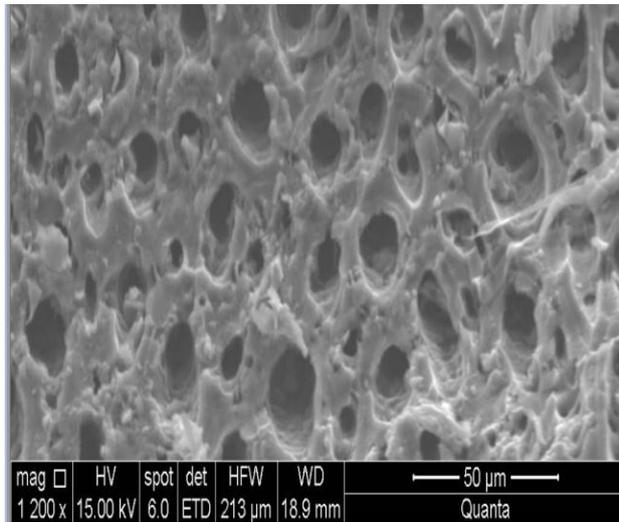
The determination of surface functions allowed us to determine the nature and quantity of functional groupings of activated carbon [23]. The results are shown in Table 2.

Methylene blue is the most accepted molecule for evaluating the capacity of the adsorbent to remove large molecules via its micro porosity. The value of the methylene blue number is in Table 2.

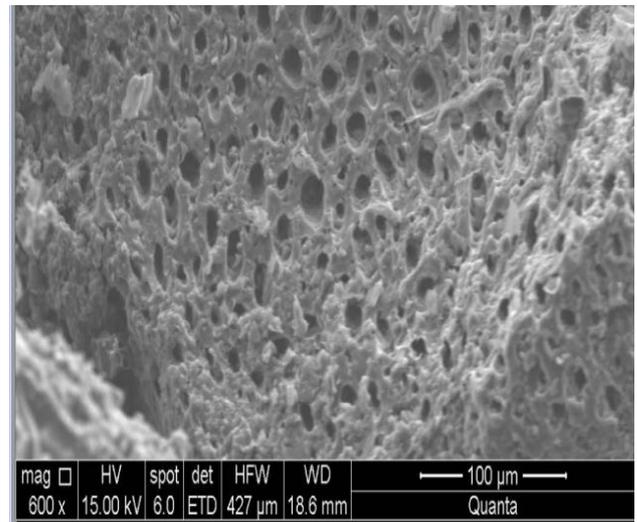
**Table 2: Adsorbent characteristics**

| MB (mg/g) | CCE (meq.g/l) | S <sub>BET</sub> (m <sup>2</sup> /g) |
|-----------|---------------|--------------------------------------|
| 40        | 0.3           | 125.863                              |

Figures 1-2 shows the images of SEM of activated carbon magnified to 600 and 1200 times. This structure is similar to the activated carbon prepared from waste coconut buttons [24].



**Figure 1:** SEM micrographs for AC particles x 1200



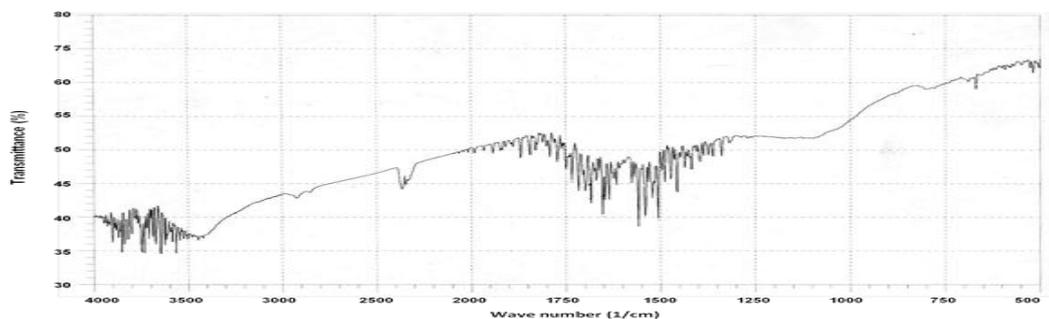
**Figure 2:** SEM micrographs for AC particles x 600

SEM analysis shows the characteristics of the structure and the morphology of the samples.

The sample has a rough texture with a large number of pores of different shapes and sizes. One can see deep cavities on the exterior surface. These cavities and pores on the surface increase the contact area and aids diffusion into the pores at the time of adsorption.

For the classification of hard or soft ligneous matter, the SEM images have been compared to those of ligneous cellulose microcrystals and to lignin [25] in the literature.

The infrared spectrum of the activated carbon has allowed us to identify eight majority signals respectively (Figure 3).



**Figure 3:** FTIR spectrum of the activated carbon

Analysis of the infrared spectrum was used to obtain information on the chemical structure and the functional groups of the operation to prepare activated carbon [26].

The main bands found in the carbon are shown in Table 3; the IR analysis shows the absence of sulphur and phosphorus groups in the structure of the carbon. One can observe the presence of different oxygen groups, mainly carbonyl, alcohol and aromatic groups.

**Table 3: the functional groups in FTIR spectrum**

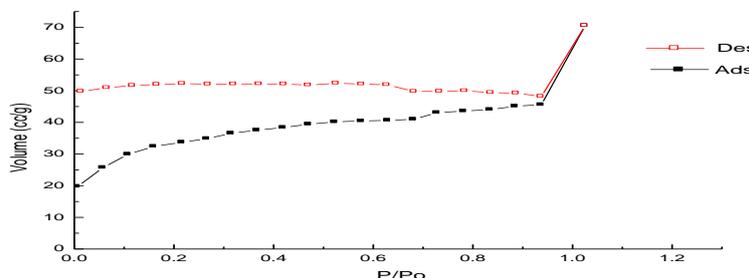
| Wave Number (cm <sup>-1</sup> ) | The bands                                                                     |
|---------------------------------|-------------------------------------------------------------------------------|
| 3400                            | Corresponding to N-H amine and imine (valence).                               |
| 2900                            | Corresponding to the C-H vibrations in methyl and methylene groups (valence). |
| 2350                            | Corresponding to C≡N nitriles (valence).                                      |
| 1570                            | Corresponding to the N=O (valence).                                           |
| 1700                            | Corresponding to C=O aldehyde and acetone groups (valence).                   |
| 1091.6                          | Corresponding to C-C groups (valence).                                        |
| 1450                            | Corresponding to C=C aromatic (valence).                                      |
| 1320                            | Corresponding to C-O alcohol, ether groups (valence).                         |

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

The activated carbon has a very micro porous internal structure. Knowledge of the type of nitrogen adsorption isotherm permits the classification of the activated carbon studied.

In figures 4 are shown the nitrogen adsorption-desorption isotherms on activated carbon. The analysis of these results permits the following observations:

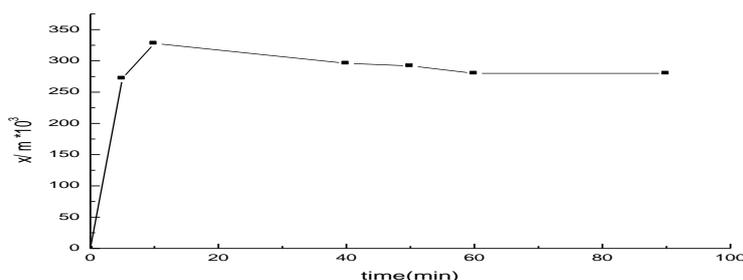
For carbon, the obtained isotherm is of type I in the BRUNAUER classification superimposed a type IV.



**Figure 4: Adsorption and desorption isotherms of nitrogen at 77°K on carbon**

**The effect of contact time**

The effect of the agitation time on the suppression of phosphate pollutants is shown in figure 5 at a fixed concentration (11mg/l).



**Figure 5: Influence of contact time on total adsorption of phosphates.**

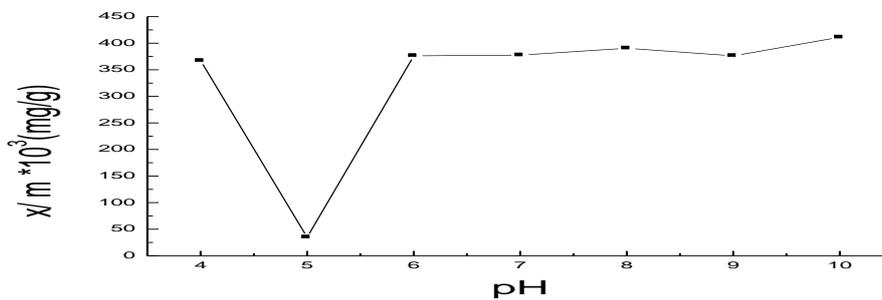
A good quantity of phosphorus is eliminated by the carbon in the first 5 minutes of contact time. This phase corresponds to a transfer of the adsorbate in liquid phase to the surface of the material. This phenomenon noted during the first minutes of the reaction can be interpreted as the start of adsorption, the number of available active sites on the surface of the adsorbent material and is higher than the reaction at sites still available later. The second part is slower. This phase corresponds to the establishment of an equilibrium between the adsorption speeds and desorption.

A time of 60 - 90 minutes the equilibrium has been considered an optimal time.

**The effect of pH**

The pH is an essential parameter to take into account in the process of adsorbing phosphorus pollutants since it acts on the ionization state of the surface of the adsorbent [27].

The figure 6 gives the Influence of pH on total adsorption of phosphates.

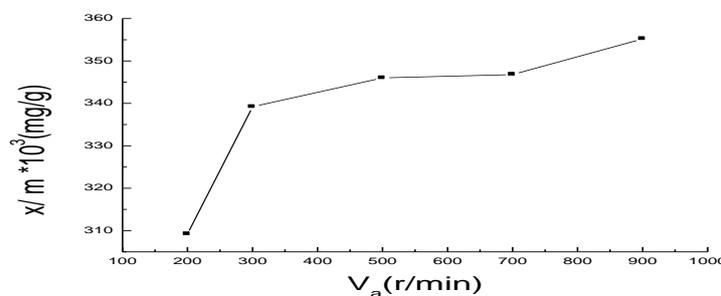


**Figure 6: Influence of pH on total adsorption of phosphates**

In the range pH=4 to pH=6 the maximal adsorbed quantity is  $375 \times 10^{-3}$  mg/g. With pH=5 the quantity adsorbed goes to a minimal 37.5mg/g. We therefore deduce that the availability of sites available to fix pollutants is dependent on pH.

Activated carbon has an amphoteric character [28]. So according to the pH of the solution the surface can be positively or negatively charged [29]. The cell wall of activated carbon contains a large number of surface functional groups. The dependence on pH of pollutant adsorption can largely be a function of the type and ionic state of the functional groups and of the adsorbate chemistry in the solution of the number and intensity of negatively charged active sites. This is due to the electrostatic attraction between the negatively charged pollutant and the positively charged surface of the adsorbent [27].

**Influence of the agitation speed**



**Figure 7: Influence of agitation speed on total adsorption phosphates.**

The agitation speed was aired between 200 and 900 rotations per minute. The results presented in figure 7 show that increasing the agitation speed to 500 rotations per minute increases the phosphate pollutants adsorption capacity. Above 500 and up to 700 rotations per minute the adsorption capacity remains

constant showing that there is an optimal agitation speed to maximize the contact between activated carbon particles and the molecules of phosphate pollutants. Above 700 rotations per minute, the adsorption capacity increased. The optimal agitation speed is sufficiently weak to not disrupt the adsorption forces.

### CONCLUSION

This study was carried out in three stages. The first is the production of activated carbon from natural ligneous cellulose "date stones". The second stage was the characterization of the obtained carbon atoms. The third stage was the application of activated carbon to the purification of wastewater in order to eliminate phosphorus. The specific surface and surface functions can be correlated. The total of phosphorus was adsorbed relatively less well onto carbon with a contact time of 90 minutes. Both contact time during agitation and pH have a positive influence on the adsorption capacity. The purification yield of activated carbon on pollutants is very important.

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