Recovery of Lignocellulosic Waste from Date Palm in Activated Carbon

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Abstract: *The objective of this study is to evaluate ligno-cellulosic biomass in activated carbons prepared from date palm waste from traditional palm groves of the south-west of Algerian Sahara: petioles, floral handles, fibrillum and spathes, using a simple pyrolysis process 450°C preceded by chemical impregnation with 40% phosphoric acid.*

The characterization demonstrates that the mass yields of activated carbon are 51,11± 3,03; 39,98± 3,23; 46,99± 1,96 and 43,79±1,41 % respectively. The iodine index are 247.46 ± 80.76; 786.78 ± 21.98; 596.43 ± 21.98; 494.93 ± 38.04 mg/g respectively.

A test for the absorption of activated carbons was evaluated by the nitrate removal test. The nitrates quantities adsorbed by the active carbons are 94.68, 95.8, 87.84 and 87.72 (mg/g) respectively. The nitrate removal yields were 47.34; 47.9; 43.92 and 43.86%, respectively. Our results show that activated carbon from petioles and floral stems have the highest amounts of adsorbed nitrate, which are correlated with the highest removal efficiencies.

Keywords: *biomass, date palm, activated carbon, characterization and adsorption of nitrates.*

1. Introduction

Today, the growing demand for adsorbent materials to protect the environment is of particular interest particularly in the manufacture of activated carbon from unconventional materials, particularly from plant waste such as food crop residues [1]. The first activated carbons uses were described well before 1550 BC on an Egyptian papyrus and much later around 400 BC by Hippocrates, mainly for medicinal use. In the 18th century, active carbons from blood, wood and bone were used for the liquids purification by filtration or sedimentation [2]. At the beginning of the 19th century the discoloration capacity of charred bones was applied in the sugar refining industry in England [2],[3]. At the beginning of the 20th century, the first processes were developed to produce on an industrial scale activated carbon meeting the requirements of the applications targeted.

Thus, manufacturing methods have improved and the Ostreijko's work [4] has been the starting point for the two basic methods of activated carbon production by physical and chemical activation. Activated carbons global annual production has been estimated at 420 000 tones [5] and according to world market forecasts, annual demand growth of 10% is expected to reach a market of 3 billion dollars in 2017 [6].

In recent years, many studies have focused on the residues valorization from agricultural and agro-industrial sectors in active coals such as rice husks [7], olive [8], cherry [9], dates pits [10], peanut [11], almonds [12],[13] and coconut shells [11], [14] and [15]. In Algeria, the date palm occupies an area estimated at 167,000 hectares for a palm trees number estimated at more than 18.6 million palm trees [16]. Phoenicicultural areas especially the date palm Phoenix dactylifera L., generates significant waste quantities which can constitute a significant agricultural waste source.

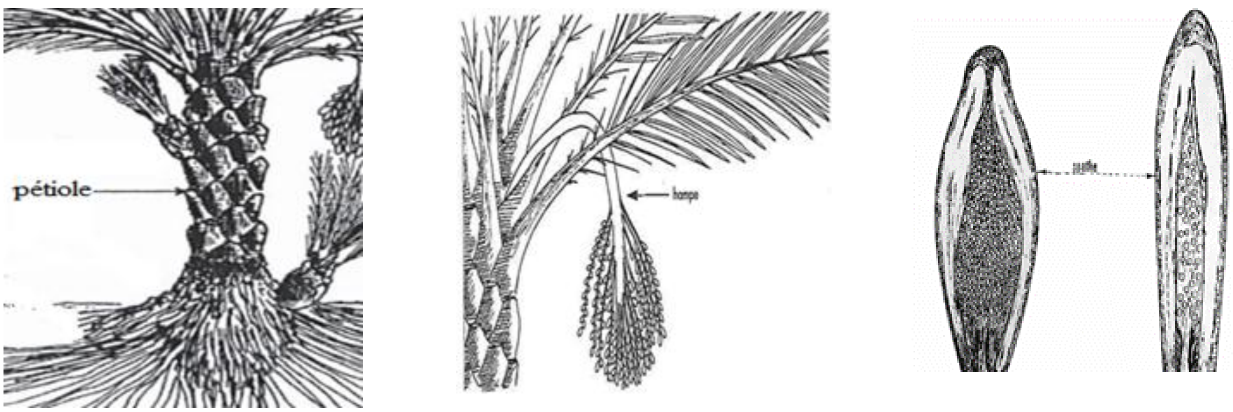
Such by-products corresponding to this loss are nevertheless likely to be of considerable economic interest. It is then important to value such ligno-cellulosic biomasses, which are inexpensive and available in large quantities in phoenicicultural areas. In the south-west of the Algerian Sahara, the area reserved for plant-growing is 27,804 hectares with more than 3 million date palms [17]. The by-products are available with a very appreciable tonnage justifying their valorization by biotechnological processes adding added value to them. In a context of sustainable development, the present study is a valuation of local lignocellulosic biomass into activated carbon. Our choice was based on four different substrates from the date palm and available in large quantities in traditional palm groves: petioles, floral stems, fibrillum and spathes.

The aim of the present study is to produce activated carbon by chemical activation. Numerous studies report that chemical activation with phosphoric acid results in activated carbons with a better efficiency for the removal of organic and inorganic micro pollutants [18], [19]. We therefore chose chemical activation using phosphoric acid (H3PO4) as a chemical activator. The activated carbons obtained were characterized and their performances were evaluated by the nitrate adsorption test.

2. Materials and Methods

2.1. Vegetable Substrate

The vegetable substrate represented by the waste of the date palm: the petioles, the floral handles, fibrillum and spathes come from traditional palm groves in the southwest of the Algerian Sahara, 2017's harvest (Fig 1). The biomass used was washed and ground with a micro-grinder and sieved with a (0.5 mm) sieve. The biomass powders are stored in hermetically sealed glass bottles.



a b c

Fig.1 different biomasses: petioles (a); Floral handles (b), and spathes (c, [20])

2.2. Preparation of Activated Carbon

2.2.1. Chemical activation with phosphoric acid

10g of the raw sample, are mixed with 20g of the phosphoric acid solution H_3PO_4 (40% by mass) and kept under stirring for 8 hours. Afterwards, the samples are placed in an oven for 24 h at 110 ° C.

2.2.2. Pyrolysis

The samples are placed in an oven at a temperature of 450 °C for one hour. The products obtained are washed with distilled water several times until the pH reaches more than 6.5. Then dried at 110 °C for 24 h [21].

2.2.3. Characterization of activated carbon

Mass yield determination

Yield is an important quantitative characteristic for active carbons. It reflects the loss of mass of the biomass during its pyrolysis. The expression of the mass yield is given by the following formula [11].

$$\text{Mass yield } (\%) = \left(\frac{M_F}{M_i}\right) * 100 \qquad (1)$$

Where:
M_f: weight of the activated carbon obtained
M_i: weight of the biomass powder (or raw materials).

Determination of iodine index (In)

The iodine index makes it possible to measure the microporosity of an activated carbon up to 2 nm, the higher its value, the greater the adsorption affinity of the material for small molecules [22]. The iodine index makes it possible to measure the microporosity of an activated carbon up to 2 nm, the higher its value, the greater the adsorption affinity of the material for small molecules [22].

$$In = ((Vb - Vs)\,N\,(126.9)\,0.15)/M \qquad (2)$$

Where:

In : The iodine index in (mg/g)

(Vb-Vs) : Difference between the titration results in the blank test and the adsorbent test in (ml0.1N of sodium thiosulfate)

N : Normality of the sodium thiosulfate solution in(mol/l).

126.9 : The atomic mass of iodine.

M : Mass of the adsorbent in (g)

Elimination of nitrates by adsorption.

The nitrates are reduced to nitrites by a solution of hydrazine in an alkaline medium and in the presence of copper sulphate as catalyst. The nitrites are then assayed by colorimetry: diazotization with sulfanilic acid and capulation with α-Naphtylamine.

The nitrate adsorption test was carried out in synthetic solutions of distilled water by adsorption on activated carbon at 0.05 g. A stock solution of nitrates at 100 mg/l was prepared by dissolving potassium nitrates (KNO3). Different standard solutions of concentrations between 5 and 100 mg/l of nitrates have been prepared. The optical densities were measured by the UV-visible spectrophotometer at 520 nm. From the calibration curve, residual nitrate levels (mg/l) were determined [24].

3. Results and Discussion

3.1. Mass yields

The mass yields of the activated carbon of the substrates: petioles, floral handles, fibrillum and spathes are respectively 51.11 ± 3.03; 39.98 ± 3.23; 46.99 ± 1.96 and 43.79 ± 1.41 (%) (Fig. 2).

The highest mass yield of the activated carbon was 51.11% for the petioles, followed by the fibrillum of 46.99%. while the lowest one was of the floral handles of 39.98%.

With the same activating agent (H3PO4), a mass yield of 59% was reported on the olive-seed [25], approaching the petiole mass yield of 51.11% and the yields between 38- 41% on sorghum grains [26] approaching mass yields of floral handles and spathes of 39.98 and 43.79% respectively.

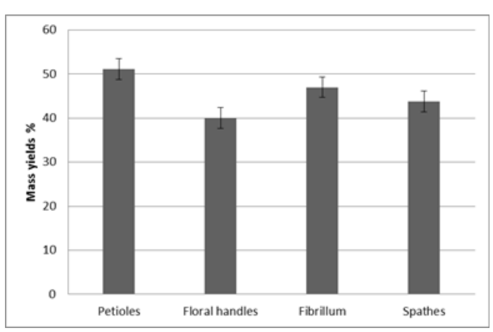


Fig. 2 Mass yields of the various activated carbons

3.2. Iodine index

The iodine index of the activated carbons from the substrates: petioles, floral handles, fibrillum and spathes are respectively 247.46 ± 80.76; 786.78 ± 21.98; 596.43 ± 21.98; 494.93 ± 38.04 mg/g .

Under the same operating conditions, with the same chemical agent (phosphoric acid) with a concentration of 40% and a pyrolysis temperature of 450-600 ° C, an iodine index of 787 mg/g was reported on an activated carbon from Shells of coconut [27] which approximates that of the floral handles whose iodine index is 786.78 mg/g.

The iodine index of activated carbon from fibrillum of the order 596.43 mg/g is close to that of activated carbon produced from a mixture of rice husks and coffee chaff, of iodine index is 590.55 mg/g [28]. The spathe iodine index of 494.93 mg/g was reported in rice husks with an iodine index of 495.30 mg/g [28]. The iodine index of activated carbon in petioles of the order of 247.46 mg/g is quite similar to that found in activated carbon from green algae of 305.70 mg/g (Fig. 3), [29].

There is therefore a proven correlation between the iodine value and the specific surface area. It has been established that the iodine index gives an estimate of the specific surface area [10], indicating the adsorption capacity in the micropores [30]. The activated carbon from the floral stem shows the highest iodine index of 786.78 mg/g which would reflect a very high adsorption capacity.

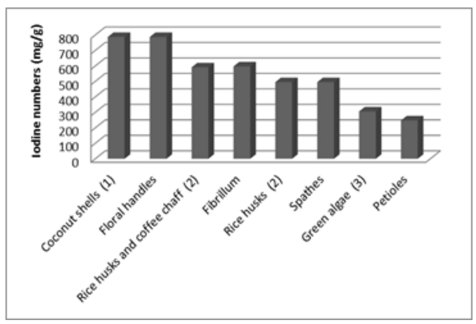


Fig. 3 Index of iodine of the active carbons of the various substrates compared with those resulting from different biomasses and under the same operating conditions. (1: [27], 2: [28], 3: [29])

3.3. Adsorbed nitrates quantities

The adsorbed nitrates quantities by the active carbons from petioles, floral handles, fibrillum and spathes are respectively 94.68; 95.8; 87.84 and 87.72 (mg/g) (Fig. 4).

The absorbed nitrates highest amount was that of activated carbon from the floral handles of 95.8 mg/g followed by that of activated carbon from petioles of the order of 94.68 mg/g.

Under the same operating conditions, studies [31] and [32] reported adsorbed nitrates quantities with adsorbent materials: functionalized chitosan beads and chitosan hydrogel beads of the order of 90 mg/g and 92.1 mg/g respectively, which approximates the amounts adsorbed by the active carbon of the floral handles and petioles of the order of 95.8 mg/g and 94.68 mg/g.

On the other hand, the adsorbed nitrates quantities by the active carbons of fibrillum and spathes of 87.84 and 87.72 (mg/g), respectively, approach that reported on another chitosan adsorbent material: $Fe3O_4/ZrO_2$/chitosan, of the order of 89.3 mg/g [31].

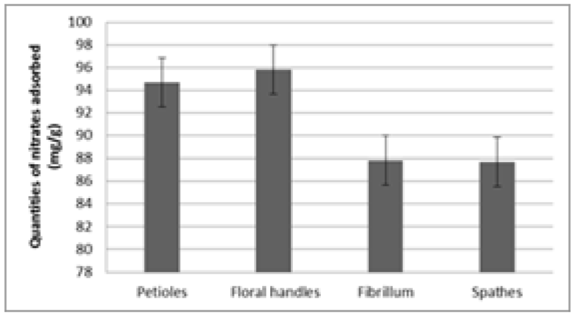


Fig. 4 Quantities of nitrates absorbed from the various activated carbons

3.4. The nitrate removal yields

The nitrate removal yields by the active carbons from petioles, floral handles, fibrillum and spathes are respectively 47.34; 47.9; 43.92 and 43.86 (%) (Fig.5).

The highest nitrate removal efficiency was obtained in the floral handles of 47.90%, which corresponds to the lowest residual content of 52.1 mg/l. The lowest nitrate removal yield was obtained in the spathes of 43.86%, which corresponds to the highest residual content in the order of 56.14 mg/l. The highest removal yield of 47.9%, corresponding to an initial nitrates concentration of 100 mg/l.

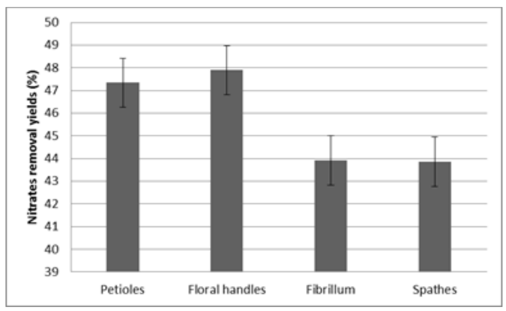


Fig.5 Nitrate removal yields of different activated carbons

4. Conclusion

Our study shows that the iodine index of the active carbons of the four biomasses are between 247.46-786.78 mg/g. The iodine, active carbons of the floral handles and fibrillum indexes of 786, 78 and 596.43 (mg/g) respectively are the highest, indicating an attractive absorptive capacity.

However, the nitrate adsorption test revealed that the best removal yields were 47.9% and 47.34%, respectively, of active carbons from floral handles and petioles. This correlates with the adsorbed nitrate quantities, the highest of which are active carbons from floral handles and petioles with amounts of the order of 95.8 mg/g and 94.68 mg/g respectively. This could be explained by the fact that the active carbon from the floral handles and the petioles are in the form of powder, unlike the activated carbon derived from the fribrillum. Studies report that powdered activated carbon is characterized by a specific surface area greater than the specific surface area of the activated carbon. This may explain why activated carbon powder is a better adsorbent. Thus, the use of these activated carbons, derived from ligno-cellulosic biomasses, as low as adsorbent could be a promising prospect in the treatment of industrial wastewater.

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