Characterization of activated carbon prepared from lignocellulosic natural residue: -Example of date stones-

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Abstract

The objective of this study is the characterization of activated carbon prepared from a lignocellulosic natural residue which is a vegetation waste "stones of dates" of the south of Algeria. After the preparation of the raw material for production, three types of carbon are pointed : a carbonized carbon at 600°C, the two others are chemically pre-treated the first one pre-treated with the nitric acid (10%) and the second with the phosphoric acid (1/1) before their carbonization at 600°C. Various results of characterization (rate humidity and ashes, specific surface, porous volume etc.) showed that the obtained carbons are comparable with those industrially prepared and could then be tested for example in the process of water treatment.

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1. INTRODUCTION

The increasing interest of world carried to the protection of the environment from the solid waste induced by the various activities and human transformations, aroused the attention of the industrial to find the technical methods to reduce if not to valorise this waste. For the case of the lignocellulosic residues "stones of olive, fish, the shell of almonds etc", the producers found applications in the production of activated carbon [1, 2]. These carbons are used for water treatment, purification of products, adsorption of gas etc. [3, 4]. However, the uses of these filter supports or adsorbent in the cited domains necessitated the knowledge of structure and texture of prepared material for example its humidity, rate of ash, pH, specific surface, porous volume etc. The knowledge of these parameters of characterization helps the explanation of the phenomena which govern the efficiency and the durability of used carbon [5, 6]. In order to valorise local materials to activated carbon, we used like precursor the date stones coming from the factory of dates paste in the south of Algeria in the locality of El-Oued. The carbons pointed by this production are of three types : the first a carbonized carbon at 600°C, the two others are chemically pre-treated, one with the nitric acid at 10 % followed by carbonization at 600°C and the other with the phosphoric acid (1/1) followed by carbonization at 600°C. The characterization of obtained carbons is realized in the second step.

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2. MATERIALS AND METHODS

2.1. Preparation of the activated carbon and chemical pre-treatment

The date stones were abundantly washed with distilled water then dried in the drying room at 105°C during 24 hours. Then they are ground and filtered to retain only the fraction including between 0.5 and 2 mm. The retained grains are chemically pre-treated before carbonization. This chemical activation can also be done after carbonization [7]. The procedure consists to introduce into a reactor, a mixture containing a determined mass of the selected fraction of date stones with acid oxidant: nitric at 10% or phosphoric concentrate (1/1). The reactor is provided with a thermostat, a refrigerant, a thermometer and an uninterrupted agitation. The reaction is maintained at 100°C during a time of contact of 1 hour. The beginning of the contact time is fixed as from the moment when the temperature reaches 100°C. Once activated, the date stones are recuperated from reactor to be dried in the drying room at 105°C during 24 hours then preserved from the air in closed bottles until the tests of carbonization.

Carbonization is realized in the enclosure of a tubular oven (Cyol) preheated at 600°C under water steam current. This temperature is maintained during 3 hours to obtain a dry residue exempt from resins or other compounds not carbonaceous. It should be noted that the oxidizing capacity of carbon dioxide can be also used, with much success [8]. The possible residues of carbonization are eliminated by an abundant washing with the hydrochloric acid (10%) and distilled water under reflux until neutralization from the rinsing water by regular checking of pH. This protocol used by Anundo Polania [7], permitted to clean the microporosity of an activated carbon prepared from coconut. Before undertaking applications in adsorption tests of pollutants or others, carbon thus treated is dried in the drying room at 105°C during at least 8 hours.

2.2. Characterization of obtained carbons

The characterization of carbon carbonized at 600°C (CAP1), chemically treated with the nitric acid (CAP2) and phosphoric acid (CAP3) required the use of several methods, spectroscopic and volumetric. The parameters pointed by this study are: humidity, the rate of ash, pH after preparation and washing of carbon. We highlighted more particularly the elementary analysis which is realized by the spectroscopy x-rays with photoemission (XPS), the specific surface (SBET) which is determined on a Micrometrics apparatus (ASAP 2010) by adsorption of nitrogen at 77°K according to the traditional method of Brunauer Emmet and Teller or BET [9]. Porous volume (Vp) is deduced from the adsorption isotherm of nitrogen in the zone of capillary condensation. The Zeta potential or hydrodynamic potential of shearing delimiting interstitial free water and water related to the particle is measured on a Zetameter 3000 HS of Malvern instrument. Measurements are realized on samples of 200mg of powder activated carbon in 50 ml of distilled water at 25°C.

The determination of total acidity and alkalinity of carbons were realized according to the method of Boehm [10]; the acid groups (carboxylic acid, lactones, phenols and carbonyls) are neutralized by a solution of 50 ml of NaOH (0.05 M) for 5g of carbon; altogether is agitated during 24 hours; after filtration, soda is dosed by 0.025 M of HCl. The basic groupings are neutralized by a solution of HCl (0.03 M), the excess of acid is dosed by 0.02M of NaOH. The carbon dioxide dissolved in the water of preparation of the solutions, susceptibility to distort measurements was eliminated by boiling before the setting in contact with carbons. For more precautions, all the samples are maintained under atmosphere of nitrogen during all these experiments of measurement of the groupings of surface. Finally in order to detect if possibly differences in morphology in the prepared carbons, photographs were taken using an electron microscope "Joel Jem 100B" having an accessory of sweeping (ASID) and an analyzer EDAX (Energy Dispersive Analysis of Analysis of X Rays).

3. RESULTS AND DISCUSSION

The knowledge of the characteristics of the activated carbon is necessary to contribute to the comprehension of many phenomena like adsorption, desorption exchanges or others. Table I represents some of the most important characteristics. The obtained results show that the pH is rather basic independently of the acid treatments because the pH measured just after carbonization at 600°C (CAP1) is 8.53. The ash, water rates as well as the parameters of texture (specific surface and porous volume) are appropriate for an industrial exploitation; many producers of
carbons make similar results [11]. We can also remark that the treatment of carbon with the phosphoric acid (CAP3) increases about ~ 47\% the specific surface and ~ 42\% of porous volume comparatively with carbonized carbon (CAP1). This result is awaited since the phosphoric acid is considered as one of the best oxidants [12]. The electrokinetic properties of the surface of carbons are a consequence of the process of activation which gave place to the formation of the oxygenated groupings on surface. The negative Zeta potential obtained is probably due to the ionization of the surface acid groupings in particular carboxylic and/or phenolic in aqueous medium and can thus be completely modified in the presence of ions determining the potential (H\(^{+}\), OH\(^{-}\)) like showed it Lafrance [13] on a powder activated carbon. For reason of this oxidation of surface and ionization, the values of Zeta potential are more negative for carbons CAP2 and CAP3.

Table 1: Some characteristics of carbons.

<table>
<thead>
<tr>
<th>Nature of carbon</th>
<th>CAP1</th>
<th>CAP2</th>
<th>CAP3</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH after wishing</td>
<td>7.53</td>
<td>6.89</td>
<td>6.68</td>
</tr>
<tr>
<td>Rate of ashes (%)</td>
<td>4.00</td>
<td>6.00</td>
<td>7.00</td>
</tr>
<tr>
<td>Rate of humidity (%)</td>
<td>9.00</td>
<td>6.00</td>
<td>7.00</td>
</tr>
<tr>
<td>Zeta Potential (mV)</td>
<td>-20.70</td>
<td>-24.20</td>
<td>-26.70</td>
</tr>
<tr>
<td>Specific area (m(^{2})/g)</td>
<td>750</td>
<td>950</td>
<td>1100</td>
</tr>
<tr>
<td>Porous volume (cm(^{3})/g)</td>
<td>0.60</td>
<td>0.75</td>
<td>0.85</td>
</tr>
</tbody>
</table>

The results of analysis of the activated carbon studied in XPS, permit to determine the chemical composition of surface, expressed in atomic percentages. The limit of detection of the elements being approximately 0.1\%. We can remark (table II) that the essential of the carbonized or activated matter is the carbon. The high percentage of this element (~ 90\%) as well as the important carbon distribution 6, 8 and 10 represent well a traditional structure of carbon [7, 8]. This interprets a good pyrolysis of the raw material or date stones. On the spectrum high resolution of carbon, we could highlight groupings CO, C=O and O-C=O. The presence of these groupings on surface or superficial functions and others is foreseeable taking into account the state of oxidation of the raw material that it is thermically (carbonization with the water steam) or chemically (H\(_3\)PO\(_4\), HNO\(_3\)).

Table 2: Elementary analysis by XPS.

<table>
<thead>
<tr>
<th>C6</th>
<th>C8</th>
<th>C10</th>
<th>CAP3</th>
<th>CAP2</th>
<th>CAP1</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>90.6%</td>
<td>90.9%</td>
<td>90.4%</td>
<td>84.8%</td>
<td>88.4%</td>
</tr>
<tr>
<td>O</td>
<td>8.1%</td>
<td>7.7%</td>
<td>6.9%</td>
<td>12.4%</td>
<td>9.6%</td>
</tr>
<tr>
<td>N</td>
<td>1.3%</td>
<td>0.7%</td>
<td>-</td>
<td>1.4%</td>
<td>1.8%</td>
</tr>
<tr>
<td>P</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.4%</td>
<td>-</td>
</tr>
<tr>
<td>Cl</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.3%</td>
<td>-</td>
</tr>
<tr>
<td>Zn</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.3%</td>
<td>-</td>
</tr>
</tbody>
</table>

The analysis of these surface functions covered the studied carbons made it possible to identify the whole of the acid and basic groupings. The results carried to the histogram (Fig. 1) make it possible to note that the quantity of the acid functions is much more important than those of the basic functions. The quantity of the acid functions compared with those basic is in ratios of 4 for CAP1, 31 for CAP2 and 48 for CAP3. On the other hand, this last carbon brings more total of acid functions than two other carbons; this is in concord with the found values of specific area.
The observations under the electron microscope with sweeping (Fig. 2) show that whatever the studied carbon, we observe a very developed porosity on all the surface of the samples with certain heterogeneity. It is clear that at the practised growths, the micropores (diameters are lower than 20 Å) and the mesopores (diameters are including between 20 and a few hundreds of Å), could not be highlighted. We can remark, the tormented aspect of surface, the existence of macrofractures and the presence of a multitude of fine particles attached to the activated carbon. These particles are much more visible on all carbons CAP2 and CAP3, they can be attributed to impurities acquired at the time of the preparation but also a reminiscence of the vegetable origin of carbon.
4. CONCLUSION

This study was realized in two steps, the first is the production of an activated carbon from a lignocellulosic natural waste “date stones”; the second step is the characterization of the obtained carbons. The good preparation of the samples for carbonization at 600°C and the chemical treatment by nitric and phosphoric acid permit to obtain carbons with physicochemical and structural properties comparable with those found in the literature but from other materials. The results of measurement of specific surfaces and functions of surface can be correlated. In the end, the possibilities of application like, in adsorption tests of pollutants or water treatment are then possible.

REFERENCES