

Elaboration and characterization of a new activated carbon obtained from oregano residue: Application in environmental field

N. Oumam¹, M. Oumam², A.K. Abourriche³, A.M. Abourriche¹, H. Hannache² and A. Bennamara¹

¹Laboratoire des Biomolécules et Synthèse Organique, Université Hassan II-Mohammedia, Faculté des Sciences Ben M'Sik, BP. 7955, Casablanca, Morocco

²Équipe des Matériaux Thermo-Structuraux et Polymères/ Laboratoire de Recherche Subatomique et Application, Université Hassan II-Mohammedia, Faculté des Sciences Ben M'Sik, BP. 7955, Casablanca, Morocco

³Laboratoire, Matériaux, Procédés, Environnement et Qualité, École Nationale des Sciences Appliquées, BP. 63, 46000 Safi, Morocco

Abstract. This study focuses on the valorization of extraction residues of medicinal plants which represent approximately 80% of the gross weight of the plant. In this context we proceeded to the transformation of "marc oregano" to a material adsorbent type activated carbon. The oregano marc, obtained after extraction of essential oils and organic compounds, has undergone a chemical activation using the phosphoric acid 85% (H₃PO₄). It is well known as precursors of lignocellulosic activating agent, allows the development of a large porosity in the activated material. The activated product has subsequently underwent heat treatment in the temperature range from 200 to 350 °C. The optimum temperature for development was set at 300 °C. The results obtained showed that the adsorbent material O₃₀₀ has developed the interesting textural properties. It is an adsorbent material like activated carbon, which presents, according to the BET method, a specific surface of 1200 m² · g⁻¹ (specific surface area of commercial activated carbon is of about 905 m² · g⁻¹). The application of adsorbent material developed O₃₀₀ in microbial decontamination of urban waste water, has revealed its effectiveness and its important adsorptive properties against pathogens pollutants from wastewater.

1. INTRODUCTION

Morocco has very significant potentials in the field of medicinal and aromatic plants (MAP). Currently, it performs the important productions of the MAP and their derivatives, which gives it a significant place in the international market. Among these we distinguish the plant of oregano which is widely used in cosmetic, pharmaceutical and food industries thanks to the flavoring, antimicrobial and antioxidant properties [1–3].

However, the extraction residues obtained from the MAP, which represent over 80% of the weight of the plant are not yet exploited. Which requires a valorization of these residues by opening a new way of exploiting these natural resources, and the transformation of these residues at activated carbon and applying it in the environmental field. It is within this context that fits the present work which has set its objectives itself: The valuation of oregano extract residues and its transformation into adsorbent material, and application of the material developed in the field of microbial decontamination of liquid effluents urban.

Activated carbons can be produced from a number of lignocellulosic precursor materials including: nuts olive, palm, peach and apricot [4,5], sawdust [6] and nut shells [7]. They are exposed to different activation methods in order to achieve a material with better adsorbent properties. The chemical activation using phosphoric acid (H₃PO₄) is widely used for lignocellulosic precursors [8, 9]. By its acid action it intervenes as catalyst of the dehydration, it can also be promoter of separation between cellulose and lignin degradation agent and units of

cellulose [10]. In addition to its role as inhibitor of carbon oxidation, phosphoric acid plays a catalytic role in the dehydration reaction. By its curing agent, it also promotes the development of a three-dimensional structure with a high porosity and with a very high specific surface.

2. CHEMICAL ACTIVATION PROCESS OF OREGANO MARC

The chemical activation process was conducted in the following experimental conditions: A mass of marc oregano (O) was mixed with phosphoric acid at different proportions. Kneading the mixture is performed at room temperature. The resulting mixture is heat-treated under air at different temperatures: 200, 250, 300 and 350 °C. Materials elaborated from oregano are called: O₂₀₀, O₂₅₀, O₃₅₀ and O₃₀₀ (numbers 200, 250, 300 and 350 indicate the temperature of treatment). The samples were then washed with water and then dried at 110 °C. The products obtained were ground and stored until used. The optimization of operating conditions showed that the mass ratio marc oregano/H₃PO₄ is equal to 1 and the temperature 300 °C are optimal conditions for preparation of activated carbon.

3. CHARACTERIZATION OF THE OBTAINED MATERIALS

3.1. (DTA/TGA) analyses of the oregano marc

In order to study the thermal behavior of studied precursor and to determine the temperature range of

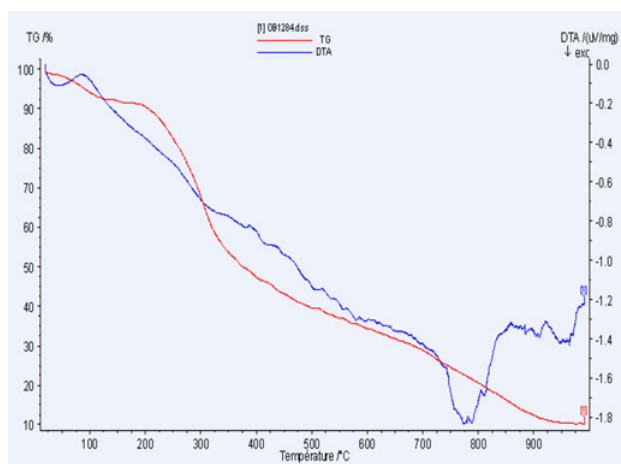


Figure 1. Thermal curves of the oregano marc (O).

Table 1. Elemental analysis of the the oregano marc (O) and elaborated materials.

Atomic %	(O)	O ₂₀₀	O ₂₅₀	O ₃₀₀	O ₃₅₀
Carbon	39	50.44	56.68	65.48	56.86
Oxygen	5.44	4.02	3.30	2.44	2.13
Hydrogen	38.59	28.13	24.92	15.69	15.96

activation, we performed a thermogravimetric analysis (DTA/TGA). The thermal and thermogravimetric analyses were carried out under argon flow with a Netzsch STA 409 apparatus. Samples of about 15 mg were heated from room temperature to 1000 °C at a heating rate of 10 °C · min⁻¹.

According to the thermogram of Figure 1, relative to oregano marc we observe three weight losses: The first, between 25 °C and 140 °C, corresponds to the dehydration of oregano marc between 25 and 140 °C. The second loss, which has a peak at around 300 °C, is due to the departure of volatile molecules (CO, CO₂ and CH₄...) during reorganizations and transformations of organic molecules. The third loss corresponds to the pyrolysis of residual carbon.

3.2. Elemental analysis

Elemental analysis was performed to determine the contents of carbon, hydrogen and oxygen, that are the main constituents of activated carbon. This analysis was conducted for oregano marc named “O” and the adsorbent materials prepared at different temperatures. The results obtained are reported in Table 1.

The results mentioned in the Table 1 show that oregano marc is relatively rich in organic carbon, which allows being a good precursor for the preparation of activated carbon. The results also show the effect of temperature treatment on the levels of hydrogen and oxygen, which decreases with increasing temperature.

The atomic percentage of carbon increases in the material elaborated until the temperature of 300 °C, then decreases beyond this temperature because of pyrolysis reactions that take place in the material subject to a higher

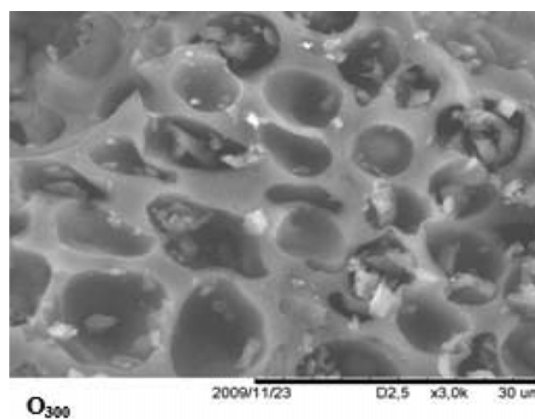


Figure 2. SEM micrograph of sample sintered at 300 °C (O₃₀₀).

temperature and which allow a rearrangement of carbon skeleton during the heat treatment.

3.3. Specific surface area

The specific surface area of O₃₀₀ material was determined based on the BET method. The measurements of adsorption and desorption were performed in an apparatus type Micromeritics ASAP 2010.

The highly developed specific surface area obtained by chemical activation of oregano marc and mainly that of elaborated material at 300 °C, shows the effectiveness of phosphoric acid and heat treatment in the opening of the porosity and improvement of the specific surface area of this product.

The sample obtained at 300 °C (O₃₀₀) present a large surface area which is of about 1200 m² g⁻¹. This value is higher than that of commercial activated carbon which has a surface of about 905 m²g⁻¹.

3.4. Determination of porosity and morphology of the obtained materials

The porosity and distribution of the pore size of each material were determined by mercury intrusion porosimetry. The apparatus used was of type IV 9500 Micromeritics Autopore.

The results obtained from the material studied, are reported in Table 2.

Table 2. Porosity of sample sintered at 300 °C.

Sample	O ₃₀₀
Average pore diameter (nm)	15.2
Porosity (%)	53.29

The internal porosity of the material is estimated at O₃₀₀ 53.29%. This material is characterized by the presence of mesopores. The texture of the adsorbent material is represented by scanning electron microscopy (SEM) shown in the Figure 2.

The Scanning Electron Micrograph shows that the activation of the cellulosic precursor in the presence of phosphoric acid followed by heat treatment has a

significant influence on the morphology of the obtained materials. The result showed a surface with rough morphological structure. The sample sintered at 300 °C show highly porous structure.

4. APPLICATION OF ADSORBENT MATERIAL O_{300} IN THE MICROBIAL DECONTAMINATION OF WASTEWATER

Previous studies [11] showed that the bacteria adhere to solid supports prepared from carbon materials. In this context, we tested the effect of the material adsorbent O_{300} against fecal coliform content in the wastewater of urban discharges. We proceeded to a filtration through a column charged with the material adsorbent O_{300} . The number of bacteria in the polluted wastewater tested was estimated at 10^{11} (CFU/ml). The filtered waters were then analyzed and compared with the starting samples and also with filtered samples through a column charged with commercial activated carbon. The results show that treated wastewater by the material O_{300} contain no bacteria (0 CFU/ml) contrary to those treated with Commercial Activated Carbon (CAC) that are still rich in bacteria pollutants ($6.4 \cdot 10^4$ CFU/ml). These interesting results show the effectiveness of the material O_{300} against water microbial pollutants.

5. CONCLUSIONS

This study provides a new way of valorization of medicinal plants extraction residues by their transformation to adsorbent materials. The activated carbon obtained at 300 °C is characterized by a developed textural properties and an important specific area (about $1200 \text{ m}^2 \text{ g}^{-1}$), which

gives it a high adsorption capacity. The results obtained in the treatment of wastewater tested, showed that O_{300} could be used as effective depolluting of wastewater thanks to these important adsorptive properties.

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