

Preparation, characterization and adsorption properties of mineral activated carbon

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Abstract — An Algerian activated mineral carbon (AC) was oxidized with different concentrations of HNO₃. The modifications in the surface chemistry resulting from these treatments have been studied by Boehm titration and FTIR. The results show that the treatments with HNO₃ increase the number of oxygenated groups on the surface of the carbons. The analysis of the adsorption isotherms of N₂, CO₂ and organic molecular probes allows estimating the extension of the two effects caused by these treatments, i.e. partial destruction of the micropores and the introduction of chemical groups that create constrictions at the entrance of the pores. These coals would be perfectly adapted to the treatment of water polluted by polar compounds.

Keywords — Activation, microporous carbons, oxidation, adsorption.

1 INTRODUCTION

Some of the applications of activated carbons, such as adsorption of polar organic compounds and metal ions, require the presence of some functional groups, i.e. oxygen complexes, on the surface of the adsorbent material [1].

The main objective of the present work is to study the influence the oxidation treatments of nitric acid solutions on the porous texture and the chemical structure of an Algerian activated mineral carbon. For this purpose, the evaluation of the textural modifications was carried out by the adsorption of N₂ at 77 K. The effect on the surface chemistry was analysed by the Boehm method and FTIR.

2 CHEMICAL STRUCTURE CHARACTERISATION

The FTIR spectra of the samples are plotted in Figure 1. It can be observed that the spectra are very similar in all cases. The differences between them lie in the relative intensity of the peaks. In general, the relative intensities of the bands increase when the concentration of HNO₃ rises. This seems to indicate that the stronger the HNO₃ treatment, the larger the amount of oxygen functionalities introduced on the surface of samples.

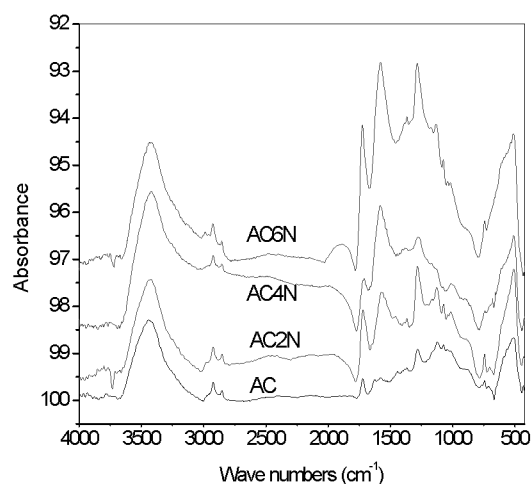


Fig. 1. FTIR Spectra of the oxidized activated carbons.

The broad bands in the spectra are expected for the functional groups that exist in a wide range of different electronic environments, and they can be assigned as follows:

- The band at 3440 cm⁻¹ can be attributed to O-H stretching mode of hydroxyl functional groups, i.e. phenolic and carboxylic groups.
- The band at 1723 cm⁻¹ is generally ascribed to the C=O stretching vibration from ketones, aldehydes, lactones or carboxyl groups [3].
- The bands around 1560-1580 cm⁻¹, more intense as the acid treatment is stronger, are generally ascribed to C=O vibration in carbonyl groups conjugated with aromatic systems [4] or assigned to aromatic

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ring stretching coupled to conjugated carbonyl groups (C=O) [3].

The results of the Boehm titration method are shown in Table 1. These results indicate that the non-oxidized sample, AC, has a mixed acidic-basic character, although the content in basic groups is significantly larger. It must be noticed that the FTIR spectrum of this sample does not show a high content of oxygenated functional groups. Hence, the basicity of this carbon is due to the oxygen free Lewis basic sites on the graphene layers and it is usually assigned to π -electrons of graphitic planes [5].

It is interesting to note that the total number of functional groups introduced is proportional to the concentration of nitric acid, as shown in Figure 2. This could be useful to determine, for any concentration of HNO_3 between 0 and 6N, the theoretical content of surface functional groups.

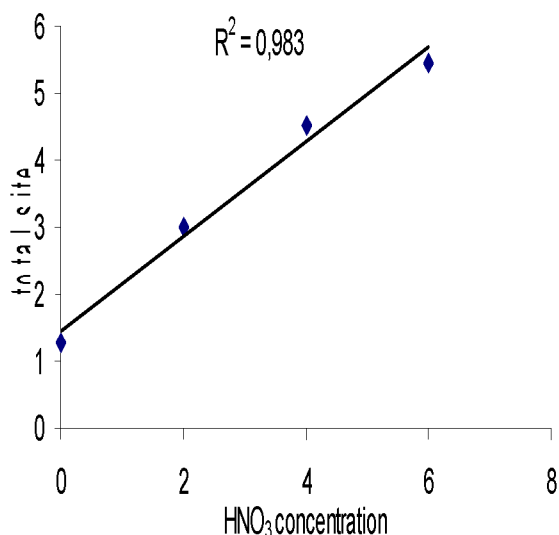


Fig.2. Evolution of oxygen site number after treatment with HNO_3 .

3 POROUS TEXTURE CHARACTERISATION

The nitrogen adsorption isotherms at 77 K obtained for the original carbon, and for the oxidized samples are shown in Figure 3. All of them are of type I in the IUPAC classification. It is seen that the treatment with nitric acid decreases the adsorption capacity of the samples. The isotherm of the non-oxidized carbon, AC, has a linear branch at high relative pressures almost parallel to the x-axis, typical of solids with a homogeneous microporosity.

The value of the saturation volume (total pore volume), V_s , is determined from the N_2 adsorption isotherm at $P/P_0 = 0.97$. It is seen that the total pore

volume and the specific surface area decrease as the oxidizing treatment is stronger: this restriction of the accessibility is caused by the fixation of oxygenated groups at the entrance of the pores. Otherwise, the treatment of AC2N and AC6N at 800 °C suggests that the acid nitric oxidation (6N) deeply modifies the texture of the original carbon AC.

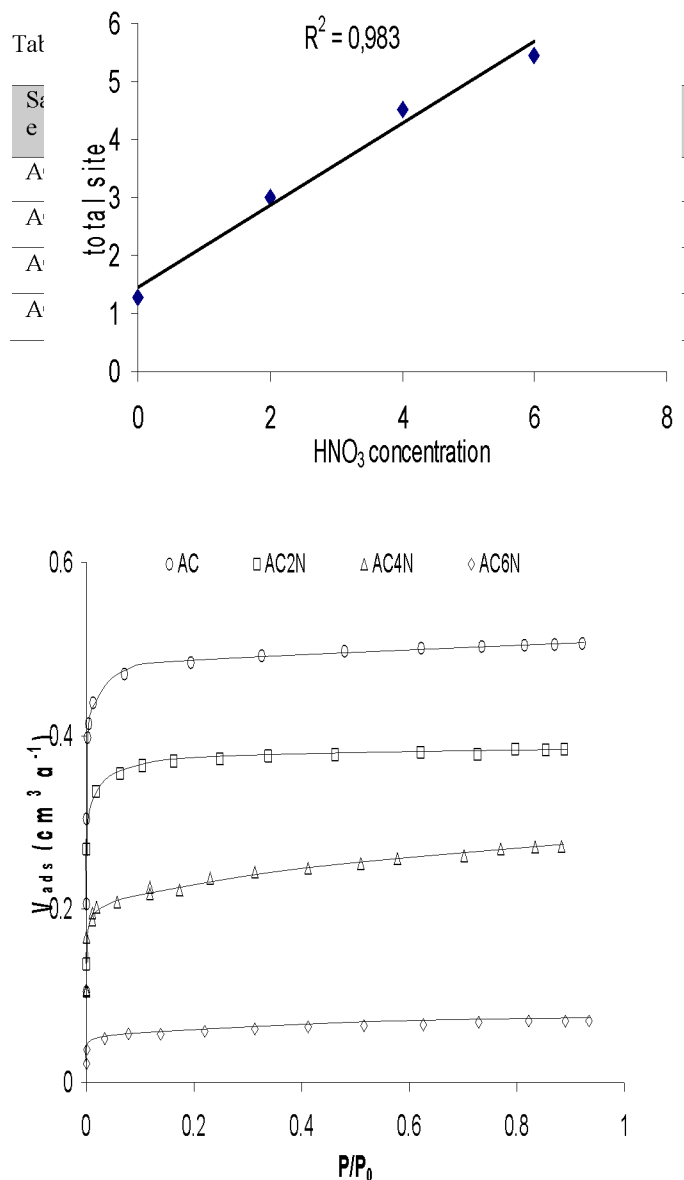


Fig. 3. Nitrogen adsorption isotherms of no-oxidized and oxidized activated carbons.

CONCLUSIONS

The treatment of the original activated carbon, AC, with different concentrations of nitric acid under strong conditions, produces an important increase in the surface oxygen containing groups. The FTIR

spectra and the Boehm method show that these functions mainly are carboxyls, lactones and phenols.

These acid treatments produce considerable changes in the adsorption properties of the samples, by two possible effects: i) the partial destruction of the micropores walls and ii) the restrictions of the accessibility caused by the fixation of oxygen containing groups at the entrance of the pores.

Table 2. Specific surface area, S_{BET} , and total pore volume, V.

Sample	AC	AC2N	AC4N	AC6N	AC2N -800	AC6N -800
S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	1240	940	550	140	1180	190
V (ml/g)	0.53	0.32	0.32	0.06	-	-

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