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KOH activated carbon multiwall nanotubes

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A protocol for chemical activation of Multi-walled carbon nanotubes (MWNTs) is presented. The modification of multi-walled carbon nanotubes is obtained by the solid / solid reaction between KOH and carbon nanotubes in a stainless cell under vacuum. The Baytubes C150 CP -Bayer[®] carbon nanotubes were reacted by KOH (MWNTs / KOH versus ratio 1 : 5). As a result, KOH reacts with the carbon nanotubes and increases the specific surface area, the ultramicropores volume, and modifies the pore size distribution.

1. Introduction : The Carbon Multi walled nanotubes, by virtue of their curved graphitic structure, small diameter (1 nm to < 100 nm) [1, 2] and high aspect ratio, possess many appealing properties including semiconducting or metallic electrical behavior, high mechanical strength, and interesting chemical and surface properties. Potential applications include mechanical actuators [3, 4], electronics [5, 6], catalysis [7, 8], sensors [9, 10], high-strength composites [11, 12], and adsorbents [13, 14].

Recently, high-yield and high-purity MWNTs were prepared by hydrocarbon decomposition on cobalt-based catalysts [15, 16]. The availability of sufficiently large amounts of high quality material permits one to analyse in detail their physicochemical properties as well as their applications in different areas. As an example, interesting results have been demonstrated when MWNTs are used as supercapacitor electrodes and for hydrogen storage [17, 18, 19, 20].

The aim of the present work was to changingt the characteristics [21, 22, 23, 24] of the nanotubes for applications of adsorbents [25, 26, 27, 28, 29].

2.1 MWNTs raw and activated :

The Multi-walled carbon nanotubes (Baytubes C150 CP - Bayer[®]) were washed in a Soxhlet extractor 6M HCl and distilled water for three days in order to eliminate the impurities. Subsequently, the Multi-walled carbon nanotubes were washed in a Soxhlet with distilled water for seven days in order to eliminate the Chlorine and finally dried in an oven at 100 °C.

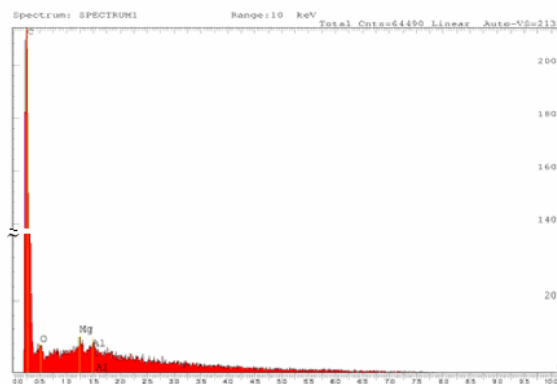


Figure (1) : EDX MWNTs pristine.

2. Experimental :

The raw [Figure (1)] and washed MWNTs were characterized by Scanning Electron Microscopy (SEM) in the backscattered electron mode using a Leo 440 microscope coupled with an energy dispersive spectrometer. The effect of washing leads to the removal of impurities : Mg, O and Al. The MWNTs were characterized by Nitrogen adsorption measurements at the liquid nitrogen temperature (77.4 K), using an Autosorb 1 LP apparatus (Quantachrome) after degassing at 200 °C for 15 hours. From this isotherm, the BET specific surface area (S_{BET}) was determined, the relative pressure range [0.01 to 0.05] was used [30]. The BJH curve was obtained using (t) thickness of Harkin and Jura [31]. The total pore volume (V_{tot}) was measured at a relative pressure of 1.1. The microporous volume (V_{micro}) was computed by applying the t-plot and the mesoporous volume (V_{meso}) was obtained by difference between the total pore volume and the microporous volume. In addition, the pore size distribution (PSD) was computed by using the Dubinin-Stoeckli method [32]. The TEM images [Figure 2, 3, 4] were realised with JEOL – 1010 microscope, 100 kV. The nanotubes possess an internal diameter of ~ 4 nm and an outer diameter of ~ 13 -16 nm with the presence of about 3 – 15 concentric tubes.

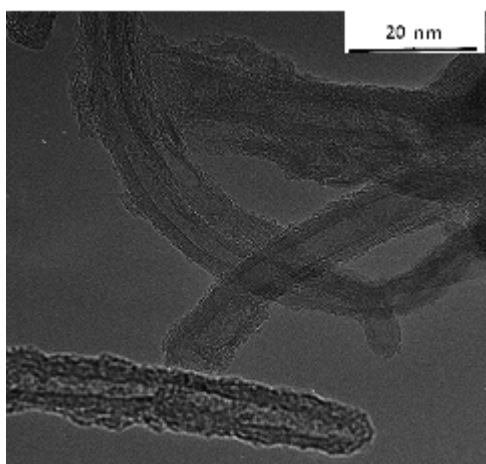


Figure (2) : TEM image of raw MWNTs.

2.2 Activation of MWNTs :

The raw purified MWNTs were mixed in a mortar with KOH in ratio 1 : 5, until they reached the consistency of a powder. The MWNTs were placed in a stainless cell (15 cm length was and 0.9 cm outer diameter). The steel cell was sealed at one end, while the other end attached to a steel valve was linked to vacuum pump. The full cell was placed in an oven at 150 °C for 12 hours in order to evaporate the water by pumping (at 10^{-4} torr) [Figure (3)].

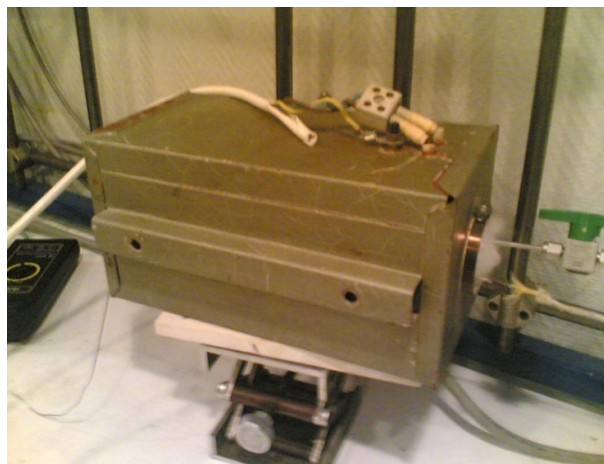


Figure (3) : Oven horizontal for degassing MWNTs Activated.

Then, the stainless cell was placed under vacuum in an oven at 750 °C for 90 min to react the MWNTs with KOH. The stainless cell was sealed under vacuum by pressing the steel capillaries [Figure (4)].



Figure (4) : Phase of the cell after cutting steel.

After reaction the steel cell was cut to obtain the activated MWNTs. To eliminate the KOH excess, the activated MWNTs were washed for one week in a Soxhlet extractor by distilled water and further dried in an oven at 110 °C.

3. Results and Discussion :

The isotherms of nitrogen adsorption at 77.4 K of the pristine MWNTs [Figure 5, 6] are of type II and typical of a mesoporous materials with an H_3 hysteresis. The BET specific surface area of the activated MWNTs is twice the one of pristine materials (Table 1). Table (1) show that the total volume remains the same for both types of nanotubes, while KOH activation increases the microporous volume and decreases the mesopores volume.

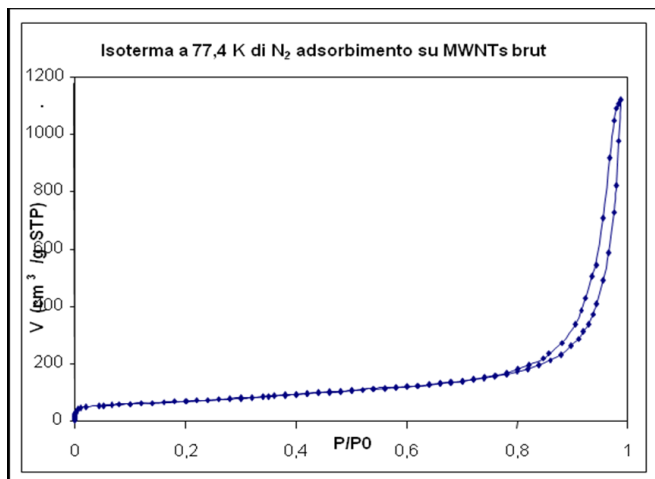


Figure (5) : Isotherm BET MWNTs Pristine.

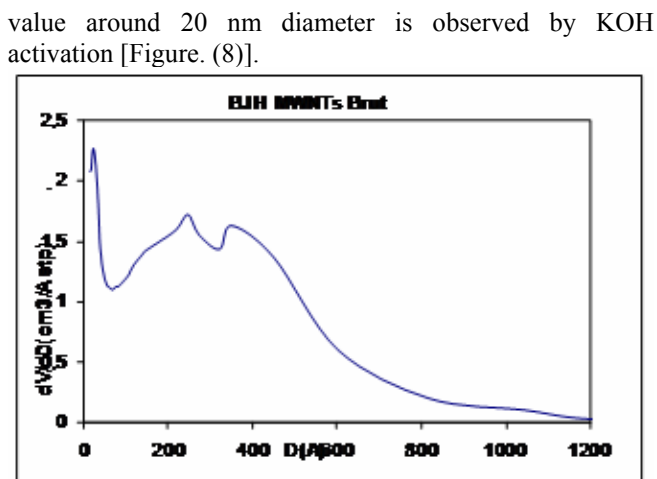


Figure (7) : BJH MWNTs pristine.

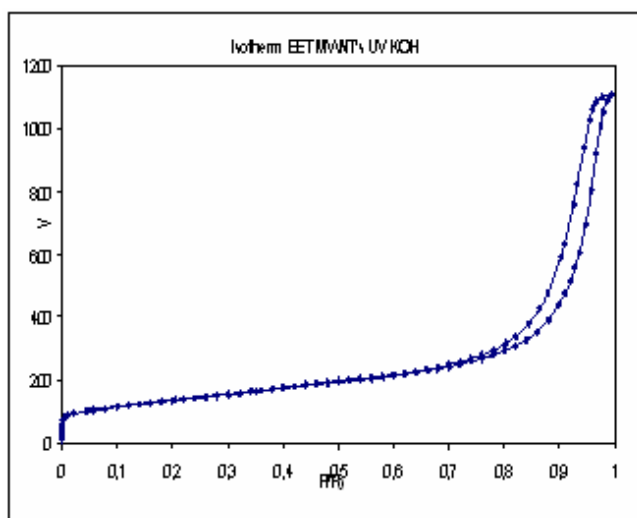


Figure (6) : Isotherm BET MWNTs activated KOH.

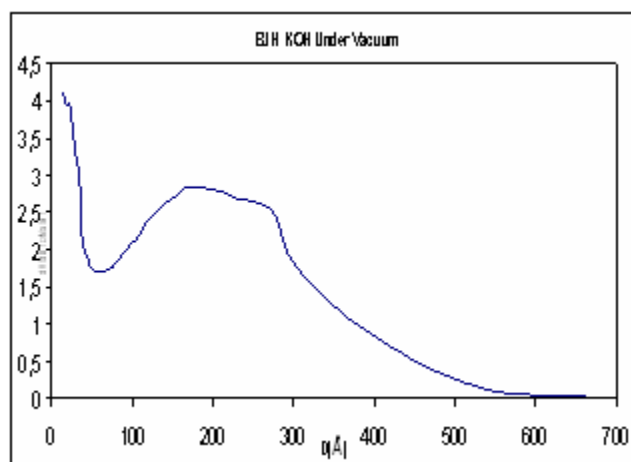


Figure (8) : BJH MWNTs activated KOH Under Vacuum.

The Dubinin-Stoeckli PSD of the raw and activated MWNTs show a drastic increase of the ultramicropores volume with pores lower then 1 nm diameter.

Table (1) : Comparison of characterization parameters of MWNTs.

	BET specific surface area (m ² /g)	V _{tot} (cm ³ /g)	V _{micro} t-plot (cm ³ /g)	V _{meso} (cm ³ /g)
MWNTs Pristine	251,3	1,7132	0,544	1,169
KOH Under Vacuum MWNTs	475,4	1,7105	0,816	0,894

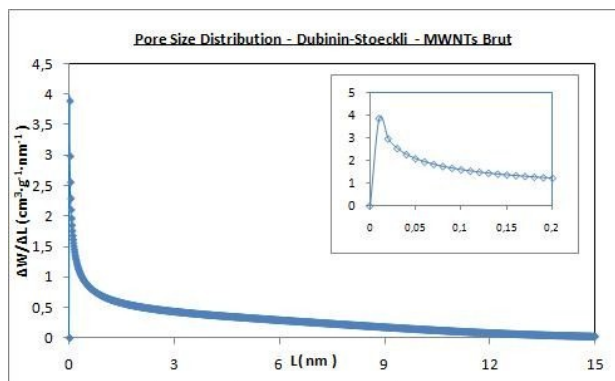


Figure (9) : BJH distribution of raw MWNTs.

Figures (7) and (8) shows the BJH pore size distribution of raw and activated nanotubes. The mesopores volume of the raw MWNTs is higher but a significant increase of the pore

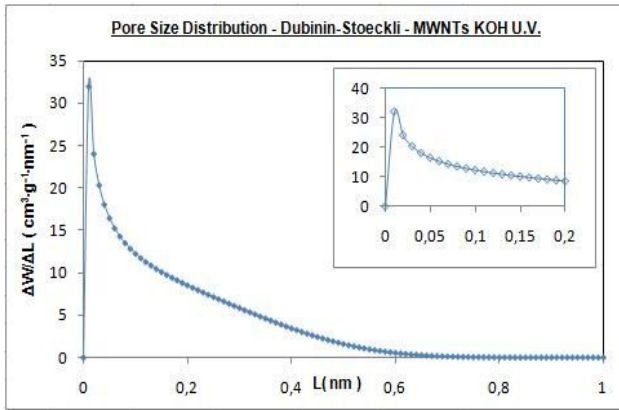


Figure (10) : BJH distribution of MWNTs activated by KOH Under Vacuum.

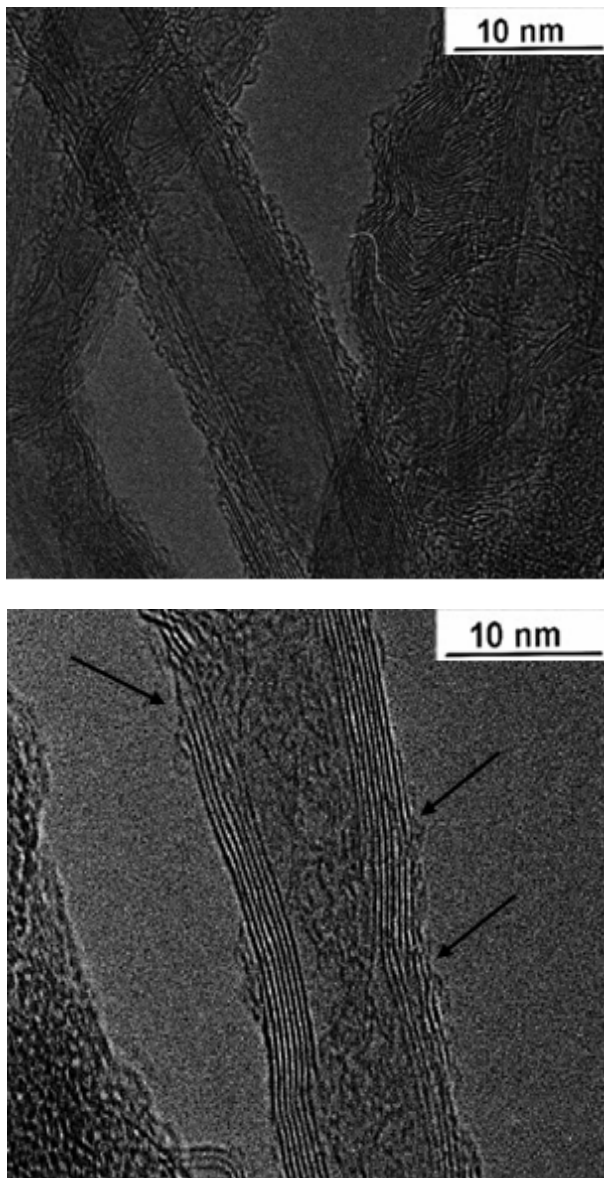


Figure (11) : Show structural defects (arrows) that appears on the nanotubes walls after KOH activation.

The raw carbon nanotubes are covered by amorphous carbon [Figure (11)]. The activation induces the oxidation of the layer that decrease the thickness of the wall. The tube walls can be destroyed partly by activation so that apertures are observed along the wall where the carbon layers were attacked by KOH.

4. Conclusion :

The KOH activation of nanotubes has been able to :

- increase the BET surface area from 251.3 m²/g to 475.4 m²/g.
- increase the mesopores volume around 20 nm diameter .
- increase volume micropores volume.

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