

Carbon monoliths for CO₂ adsorption

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In this article we present the characterization of some carbon monoliths, which have an open and permeable structure. Due to electrical and thermal conductivity of the carbon fibers these composites could be electrically desorbed. The monoliths were prepared from milled carbon fibers and a phenolic resin. The obtained monolithic composites were carbonized up to 650°C and then the composites were steam activated at 800°C. By activation, the adsorption capacity of carbon dioxide was improved. The carbon fibers composites were characterized using scanning electron microscopy, atomic force microscopy, X-ray diffraction, BET surface area analysis and volumetric measurements of gas adsorption.

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1. Introduction

Activated carbon has been widely used in many fields and can be produced from a variety of carbonaceous source materials like woods, fruit stones, nutshells, straw, synthetic organic polymers and many other organic waste materials. Recently, interest has been focused on carbon fibers activated by chemical or physical methods [1-3]. Activated carbon fibers have new properties that make them more attractive than conventional forms (powder or granule carbons) for specific applications. Activated carbon fibers are interesting for the adsorption and recovery of organic vapors, the environment protection, for removing CO_x, SO_x and NO_x from gases, and improve air quality [4-6]. Difficulties in using activated carbon fibers can be overcome by incorporating them into a composite, such as woven or nonwoven structure, felt or paper.

Carbon fibers are produced commercially from rayon, PAN and pitch. High performance fibers, such as those with high strength and stiffness, are generally produced from PAN and mesophase pitch. Isotropic fiber applications include: friction materials, reinforcements for plastics, electrically conductive fillers for polymers, filters, paper, hybrid mix, and as reinforced concrete.

The interest in using monolithic structures for chemical conversion and adsorption processes is increasing. A relatively new type of monolith is based on carbon [7]. The combined favorable properties of carbon and monolithic structures create a support with great potential in catalytic and adsorption processes.

In this article we present the obtaining process and characterization of some rigid monolithic composites with carbon fibers, which have an open and permeable structure. Due to electrical and thermal conductivity of the carbon fibers these composites could be electrically desorbed.

2. Experimental

The monoliths were prepared from milled pitch or PAN based carbon fibers and a phenolic resin. The fibers have an average length of approximately 150 μm, 200 μm, 400 μm, respectively 800 μm. The weight ratio of carbon fibers to phenolic resin is 3:1. The fibers and phenolic resin powder were mixed with water to obtain slurry. The slurry was transferred into a mold and the water was removed under vacuum. The resulting forms were dried in air at 60°C for 16 hours and after this at 150°C for 4 hours in order to produce cured monoliths [8].

The obtained monolithic composites (FCN150, FCN200, FCN400 and FCN800) were carbonized with a heating rate of 2°C/min up to a maximum temperature of 650°C and held at this temperature for 3 hours in a nitrogen flow of 500 ml/min (Fig. 1).

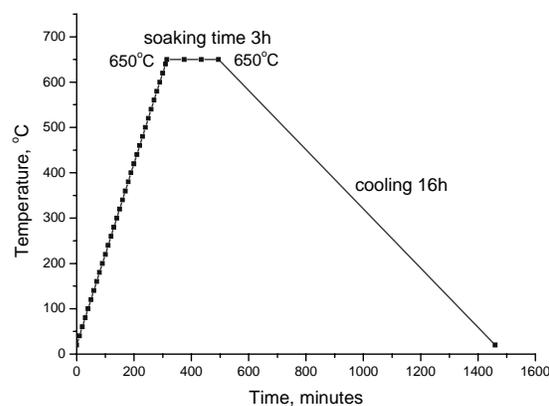


Fig. 1. Thermal treatment diagram for monolithic composites.

After carbonization, in order to increase the adsorption capacity, the composites were activated by physical methods using steam at 800°C, with 500 cm³/h flow, for 1 hour. By activation, the surface area of the composites increased and particularly the obtaining of micropores was expected, thus improving the surface area, pore volume, respectively adsorption capacity.

The properties of milled carbon fibers are presented in table 1 and the properties of phenolic resin powder are presented in Table 2. Milled carbon fibers were purchase from Asbury Graphite Mills Inc. (New Jersey, USA). Phenolic resin (novolak) powder type Steron F-VIII NVD from Dynea Chemicals Oy was used.

Table 1. Physical properties of milled carbon fibers from petroleum pitch.

Properties	PAN carbon fibers	Pitch carbon fibers		
		200	400	800
Average length, μm	150			
Fiber diameter, μm	7.4	13	13	13
Density, g/cm^3	1.75	1.54	1.54	1.54
Carbon, %	99.5%	95%	95%	95%
Resistivity, $\mu\Omega\text{m}$	14	60	60	60
Tensile strength, GPa	3.6	0.5	0.5	0.5
Young's Modulus, GPa	207	35	35	35

Table 2. Physical properties of phenolic resin powder.

Properties	
Appearance	Yellowish powder
No tamped volumetric weight, g/dm^3	350-550
Tamped volumetric weight, g/dm^3	600-800
pH	7-8.5
Softening point, °C	75-90
Melting point, °C	100-115
Solubility in acetone, ethyl alcohol, ethyl acetate	Soluble
Solubility in benzene, carbon tetrachloride, gasoline, water	Partially soluble
Rest on the 0.1 wire cloth sieve, %	max 2%

3. Results

The carbon monoliths were prepared from milled pitch or PAN based carbon fibers.

Four type of composites were obtained and characterized: FCN150, FCN200, FCN400 and FCN800, using X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM), BET surface area analysis, pore size distribution and volumetric

measurements of gas sorption.

X-Ray Diffraction analyses were performed with a D8 ADVANCE type BRUKER-AXS Diffractometer, equipped with a Cu target X-ray tube ($\lambda=1.5406 \text{ \AA}$) 40 kV/30 mA and Ni K β filter, 0.04° step, measuring time of a point 1 second.

Semiconduct AFM analyses were performed with a Scanning Probe Microscope model NTEGRA Aura. SEM analyses were performed with a Workstation Auriga Carl Zeiss.

BET surface area and pore size distribution determination were performed by physical adsorption of N₂ at a temperature of -196°C with a surface area and pore size analyzer type AUTOSORB-1 Quantachrome. The samples were degassed under vacuum ($< 10^{-6}$ atm) at a temperature of 300°C for 4 hours. Surface area was calculated by applying the BET method [9]. Also, Low-pressure carbon dioxide (CO₂) adsorption measurements up to 1 bar were performed on AUTOSORB-1 volumetric analyzer.

Volumetric measurements of CO₂ sorption were performed with a PCTPro-E&E type Sievert instrument at room temperature ($\sim 25^\circ\text{C}$) and up to a pressure of 10 bar.

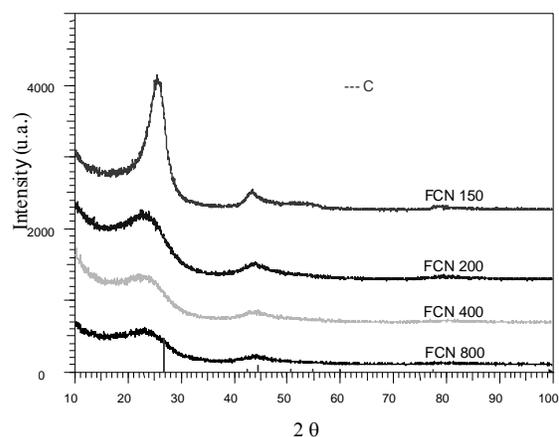


Fig. 2. X-ray diffraction patterns for non-activated composites.

Table 3. Cell parameters obtained from XRD patterns.

Sample	a [Å]	c [Å]
FCN150	2.407	7.004
FCN200	2.372	7.471
FCN400	2.352	7.385
FCN800	2.364	7.687
Turbostratic graphite (index 03-065-6212)	2.464	6.711

Table 4. The average size of crystallites calculated with Debye-Scherrer formula.

Sample	hkl	D (nm)
FCN150	(002)	2.1
	(101)	3.6
FCN200	(002)	1.2
	(101)	1.8
FCN400	(002)	1.3
	(101)	2.2
FCN800	(002)	1.1
	(101)	1.9

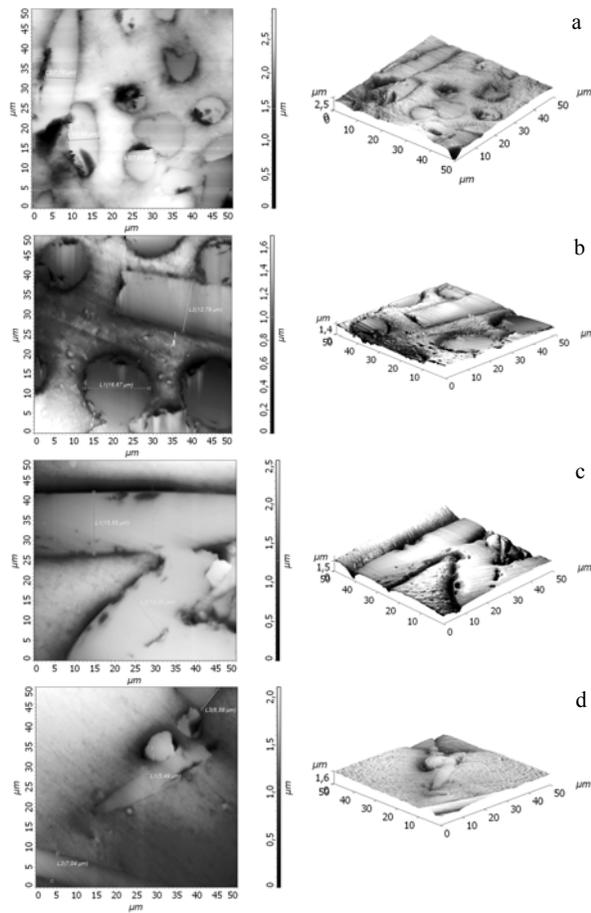


Fig. 3. 2D and 3D AFM topography of the non-activated composites: (a) FCN150, (b) FCN200, (c) FCN400, (d) FCN800.

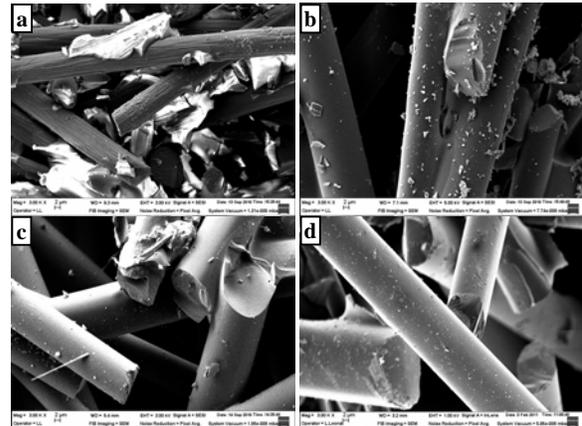


Fig. 4. SEM images of the non-activated composites: (a) FCN150, (b) FCN200, (c) FCN400, (d) FCN800.

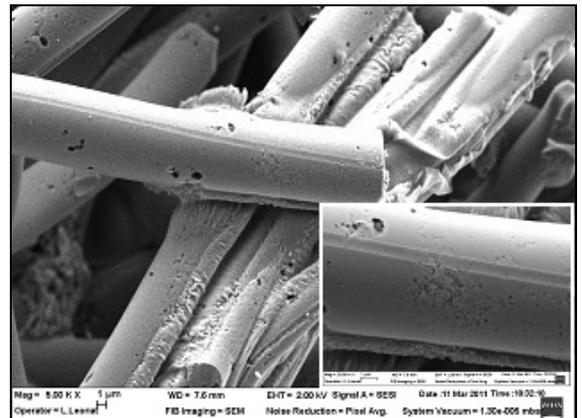


Fig. 5. SEM images of the steam activated FCN400 composite.

Table 5. Porosity characteristics of non-activated composites.

Sample	BET surface area [m ² /g]	Total pore volume [cm ³ /g]
FCN150	5.64	6.673*10 ⁻³
FCN200	10.86	7.087*10 ⁻³
FCN400	16.82	7.519*10 ⁻³
FCN800	3.46	6.425*10 ⁻³

Table 6. Porosity characteristics of steam activated composites.

Activated sample	BET surface area [m ² /g]	Total pore volume [cm ³ /g]	DR micropore volume [cm ³ /g]
FCN150	114.62	5.07*10 ⁻²	5.18*10 ⁻²
FCN200	226.37	1.17*10 ⁻¹	1.97*10 ⁻²
FCN400	379.15	1.73*10 ⁻¹	2.75*10 ⁻²
FCN800	506.08	4.45*10 ⁻¹	2.31*10 ⁻¹

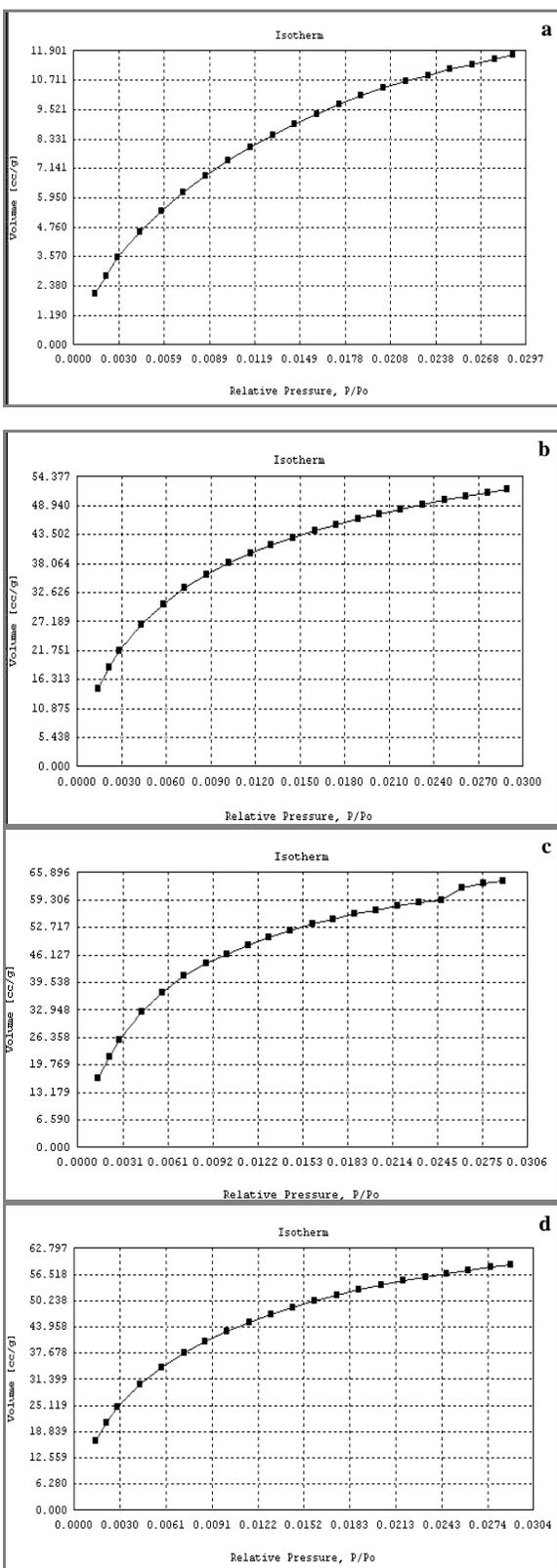


Fig. 6. CO₂ adsorption isotherms for steam activated composites: (a) FCN150, (b) FCN200, (c) FCN400, (d) FCN800.

Table 7. Volumetric adsorption of CO₂ on carbon fiber composites.

Sample	CO ₂ Concentration [moles gas / kg sample]
FCN150	17.3631
FCN200	13.5438
FCN400	35.9424
FCN800	26.5896

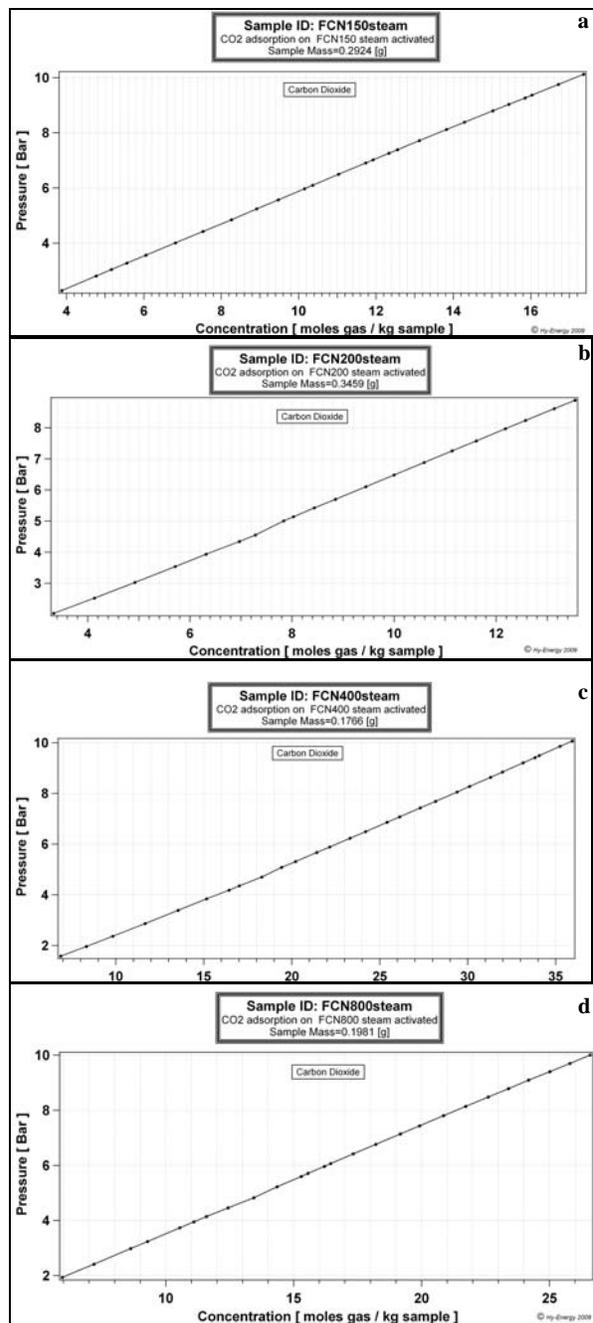


Fig. 7. Pressure-composition isotherms (PCT) for steam activated composites: (a) FCN150, (b) FCN200, (c) FCN400, (d) FCN800.

4. Discussion

Fig. 2 shows the XRD patterns of the non-activated composites FCN150, FCN200, FCN400 and FCN800. Classical analysis of XRD pattern obtained on graphite type carbon materials is based on planar disordered network model, called turbostratic model (Biscoe and Warren, 1942). In agreement with this model, carbon atoms form stacks of flat graphenic equidistant layers, parallel planes randomly translated and rotated around an axis perpendicular to the plane. Turbostratic structure can be considered as a two-dimensional structure in which graphenic planes scatter radiation independently.

XRD patterns of the composites reveal the presence of (002) line which is characteristic of turbostratic graphite. Their structure is similar to the hexagonal structure of graphite, having elementary cell parameters presented in Table 3. Table 4 presents the average size of crystallites calculated with Debye-Scherrer formula.

Fig. 3 (a, b, c, d) shows 2D and 3D topographic images of the composites obtained by atomic force microscopy. It can be seen that the carbon fibers and phenolic resin have a good compatibility. The carbonized resin provides the links between carbon fibers. The three-dimensional distribution of the fibers in the composites is random. The composites have a porous open structure.

From the SEM images (Fig. 4 a, b, c, d and Fig. 5), it can be observed the three-dimensional network composed of the carbon fibers and the carbonized novolak resin used as binder. The carbonized novolak resin bonds the carbon fibers thus providing mechanical strength and electrical conductivity of the obtained composites.

The pores which are developed at the surface of the carbon fibers after the steam activation process can be clearly seen in Fig. 5. The resultant open structure allows the free flow of fluids through the monoliths such that gases can reach the micropores where they may be selectively adsorbed. The monoliths are also macroporous, exhibiting large voids between the fibers.

Tables 5 and 6 include the results of the BET surface area and pore size distribution determinations of the non-activated and steam activated composites. For the non-activated composites, BET surface area increases according to the increase of carbon fibers length, composite FCN800 being an exception, with a surface area of 3.46 m²/g. Pore volume varies proportionally with the BET surface area, which is actually a measure of the porosity of the studied material. FCN400 non-activated composite presents the highest values for surface area of 16.82 m²/g and a total pore volume of 7.519*10⁻³ cm³/g.

For the steam activated composites, BET surface area, total pore volume and DR micropore volume vary proportionally with the increase of carbon fibers length. After steam activation, the surface area increases about 20 times in almost all types of composites. Especially for the FCN800 activated composite, the surface area increased from 3.46 m²/g to 506.08 m²/g, which is about 146 times.

Fig. 6 (a, b, c, d) shows the CO₂ adsorption isotherms at low pressure (up to 1 bar) for steam activated composites. The isotherms shape show a linear behavior in the P/Po range of 0.01–0.025, which is correspondent to the

adsorption process in micropores. Based on these adsorption isotherms, the software of the instrument used the Dubinin-Radushkevitch method to calculate the DR micropore volume, this method being used for detecting micropores in the presence of mesopores. The highest value of DR micropore volume of 2.31*10⁻¹ cm³/g was obtained for the steam activated composite FCN800.

The adsorption capacity increased from 13.5438 moles CO₂ / kg for FCN200 composite to 35.9424 moles CO₂ / kg for FCN400 composite (Table 7).

As it can be seen from Fig. 7 (a, b, c, d), by volumetric adsorption measurements, we obtain a maximum adsorption capacity for steam activated FCN400 of 35.9424 moles CO₂ / kg sample at a pressure of 10 bar.

5. Conclusions

The porous carbon fibers composites studied in this article have an interesting structure. A monolithic open porous carbon structure was obtained using the phenolic resin as binder for carbon fibers. After the heat treatment, the phenolic resin is converted to carbon that provides mechanical and electrical connection between the milled carbon fibers. Steam activation process increases both the surface area and the pore volume, so that the CO₂ adsorption capacity was increased.

The results presented above prove the fact that steam activated composites are promising for future successful applications in CO₂ adsorption.

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