ACTIVATED CARBON FOAM DERIVED
FROM TREATMENT PRODUCTS OF RDF
WITHOUT PRESSURE AND STABILIZATION STAGE
FOR REMOVAL OF POLLUTANTS FROM WATER

Ivanka Stoycheva[#], Boyko Tsyntsarski[#], Angelina Kosateva,
Bilyana Petrova, Georgi Georgiev, Kalina Miteva

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Abstract

Carbon foam is an advanced porous material with multiple high-technology applications, due to its cell structure, light weight, very good thermal and chemical stability, high thermal and electrical conductivity, as well as exceptional electromagnetic and acoustic properties. The present work aims to find suitable treatment, allowing the formation of a large number of micro- and mesopores in carbon foams, obtained by recently developed synthesis method without the use of pressure and stabilization stage. High compressive strength materials were synthesized after heat treatment up to 1000 °C. It was found that the heat treatment in the presence of water vapour of the obtained carbon foam samples allows a significant increase in specific surface area and the volume of the micro- and mesopores. This gives the possibility for successful application of the synthesized material in water and air purification, as a catalyst support, construction material, and in other fields.

Key words: carbon foam, activation, pressure, pore structure, SEM, XRD

[#]Corresponding author.

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Introduction. Carbon foams are light macroporous materials with wide range of properties as low density, high thermal stability, low thermal expansion coefficient, high sound wave absorption [1,2]. It was determined that carbon foam properties are directly connected to the nature of the precursor and the parameters of the process – temperature and pressure [3]. This gives possibility for control of bulk properties during foaming process. The effect of the precursor on the structure and properties of obtained carbon foams is essential [4-9]. Carbon foams have been tested for use as a thermal energy storage container, electrodes, for reflection of electromagnetic waves, catalyst support, adsorbent, etc. [2].

The porous structure of the carbon adsorbent is a very important factor determining its ability to retain various adsorbates on its surface. The absence or insignificant content of one of the types of pores (micro-, meso- and macropores) reduces its effectiveness. The most commonly used carbon adsorbent is activated carbon. Activated carbon obtained by physical activation contains mainly micro- and mesopores. The need for an adsorbent containing larger pores accessible to bigger molecules, bacteria and viruses, thus significantly increasing its effective surface when used in protective masks, requires the production of a carbon adsorbent with a larger number of macropores. This could be done using physical activation of macroporous carbon foam, which leads to formation of micro- and mesopores, which significantly increases the surface area. The first studies [10] of the team on the production of carbon foam from Bulgarian coal pitch modified by treatment with strong oxidants such as H_2SO_4 and HNO_3 demonstrated the significant influence of the nature of the oxidant on the chemical processes during the synthesis and formation of the resulting carbon foam. This leads to difference in the physicochemical properties of the obtained final products. Further XPS investigation of carbon foams is performed [11]. Based on the results of further studies [12], it was found that the main reason for these differences is the ability of sulphuric acid to catalyze the polymerization and polycondensation reactions during synthesis procedure. This leads to the formation of final product with denser structure. At the same time, some factors, like higher amount of volatile products, different rheology (viscosity) of the reaction mixture and delayed solidification during nitric acid treatment, lead to formation of carbon foam with more regular porous structure and lower mechanical strength. Higher surface reactivity of the carbon foam, obtained after treating the raw material with nitric acid, is a prerequisite for faster and easier physical activation of the carbon foam and further formation of micro- and mesopores in the macroporous material.

The aim of the present investigation is to find a suitable activation treatment allowing the formation of large number of micro- and mesopores, which will expand the range of size of the pores of the carbon foam obtained by a developed by us method for the synthesis of carbon foam, without the use of pressure and stabilization step, and increase the possibilities for its application.

Materials and methods. Synthesis of the samples. The raw material used is tar obtained from the heat treatment of waste biomass. Its main application was as a low calorific fuel.

Mixture of tar pitch derived from RDF fuel with softening point 70 °C and furfural (50:50 wt%) is used as precursor. Biomass tar pitch is heated up to 120 °C till melting and furfural is added with continuous stirring. The obtained mixture was treated at 200 °C with 68 wt.% HNO₃ with continuous stirring. The obtained solid product was washed with water, and then carbonized at 600 °C.

The carbonizate (CFNcarb) is heated up to 1000 °C under nitrogen atmosphere (CFN1000).

The preparation of activated carbon foam (CFNactiv) is performed by thermochemical treatment with water vapour (hydropyrolysis or physical activation with water vapour) of the carbonized samples (CFNcarb) at different temperatures for 60 min and a rate of temperature rise of 15 °C.

Methods of characterization. The elemental analysis is performed on Vario Macro Cube (Elementar Analyzensysteme GmbH) equipment for determination of C, H, N, S. Oxygen content is determined by the difference.

The morphological study is performed using scanning electron microscope FEI Quanta 250 FEG.

Mechanical tests are performed in the Technical University, Sofia.

The adsorption of iodine from solution is determined as follows. A sample of 0.10 g of activated carbon foam is shaken together with 25 cm³ of I₂/KI solution for 1 h. The adsorption of methylene blue in aqueous solution has been measured by using a method described elsewhere [13].

Textural characterization of the carbon foams is carried out by N₂ adsorption at -196 °C using Quantachrome Instruments NOVA 1200e (USA) apparatus. Before the experiments, the samples are outgassed under secondary vacuum at 300 °C overnight. The N₂ adsorption isotherms are used to calculate the specific surface area, S_{BET} and pore volumes.

Results and discussion. The amounts of adsorbed iodine into pores larger than 2.5 nm methylene blue are important adsorption characteristics of the studied activated carbon foams. They also give an idea of the porous texture of the samples, as it is well known that iodine molecules penetrate into pores larger than 1.5 nm, and methylene blue molecules, respectively, into pores larger than 2.5 nm. The data in Table 1 show the change of some parameters with the increase of the activation temperature. Adsorption capacity of the obtained activated carbon foams towards iodine and methylene blue increases significantly with increasing activation temperature. At the same time the amount of products obtained at higher temperatures is lower. Significantly higher values for iodine adsorption brings information about the higher content of pores with smaller sizes compared to meso- and macropores. This shows that the goal of activated treatment of the carbon foams has been achieved, namely the formation of a large amount of meso-

T a b l e 1

Adsorption characteristics of carbon foams activated at different temperatures

Sample	Activation temperature, °C	Iodine adsorption, mg/g	Methylene blue adsorption, mg/g	Yield, %
CFNactiv750	750	620	125	87
CFNactiv800	800	780	165	81
CFNactiv850	850	900	235	72

and micropores. An elemental analysis of carbonized and activated carbon foams was performed for an explanation of this experimental fact.

Elemental analysis of the samples shows the following results: CFNcarb (C/H=8.18) contains 90.31 wt.% C, 0.92 wt.% H, 2.52 wt.% N, 0.87 wt.% S, and 5.37 wt.% O, whereas CFNactiv850 (C/H=8.18) – 90.01 wt.% C, 0.70 wt.% H, 1.40 wt.% N, 0.61 wt.% S, and 7.28 wt.% O. Data indicate that the higher number of condensation reactions, occurring during the synthesis and carbonization of the foam precursor lead to the formation of condensed aromatic structures, which is related with high carbon and low hydrogen content. The samples have very low ash content (0.13 wt%) and demonstrate high hydrogen content, whereas sulphur content diminishes after the process of activation.

The thermograms in an oxygen atmosphere of the activated carbon foams showed very little weight loss at temperatures below 500 °C and slower weight loss at temperatures above 500 °C to 600 °C.

High compressive strength of 15 MPa for CFN1000 sample is measured, which is close to compressive strength (3–20 MPa) obtained for carbon foam samples, produced by other researchers [14, 15].

The data in Table 1 unequivocally show that the best activated sample is CFNactiv850, which has the highest adsorption capacity towards iodine and methylene blue at sufficiently high yield of the final product. For a more complete characterization of this sample, it was examined by nitrogen physisorption. Based on the obtained isotherm, important texture parameters are calculated. Figure 1 shows the nitrogen isotherm of the initial and activated sample. The calculated parameters based on the obtained isotherm are presented in Table 2.

The comparison of the isotherms of the initial and activated sample is a proof of the significant increase of the pore volume, especially of the micropores of the material as a result of the activation with water vapour. The course of the isotherm (a) shows that the activated sample is characterized by a microporous structure (steep rise at low pressures) and a small content of mesopores (small slope at higher pressures).

The main textural parameters of activated sample are presented in Table 2. The results show that before activation carbon foam does not exhibit any porosity in the micropore or mesopore range.

Fig. 1. N₂ adsorption isotherms at 77 K of the HNO₃ treated carbon foam samples before (a) and after activation (b)

T a b l e 2

Main textural parameters of the CFN before and after steam activation

Sample	S_{BET} $\text{m}^2 \text{g}^{-1}$	V_{total} $\text{cm}^3 \text{g}^{-1}$	V_{micro} $\text{cm}^3 \text{g}^{-1}$	V_{meso} $\text{cm}^3 \text{g}^{-1}$
CFNcarb	122	0.020	0.010	0.010
CFNactiv850	902	0.398	0.389	0.009

After steam activation, the opening of the carbon matrix to form a porous structure is evident in the material – activated carbon foam demonstrates an open structure of interconnected pores with a micro/mesoporous network.

The short time for the steam activation (ca. 60 min) should also be highlighted, compared to the much longer times usually employed in the manufacturing of activated carbons. Despite this, the resulting activated carbon foam exhibited high surface area of $902 \text{ m}^2 \text{g}^{-1}$ and a porous volume of $0.40 \text{ cm}^3 \text{g}^{-1}$. Such high surface areas in carbon foams have been reported only after chemical activation of carbon foams using high activating agent ratio [1,2].

The images in Fig. 2 show the differences in the structure of the carbonized carbon foam as a result of the activation with water vapour.

It can be seen that the steam activation leads to the formation of a large number of pores of smaller size, and in the same time, significant amount of macropores remain in the activated sample. After activation, final material containing significant amount of all types of pores (micro-, meso- and macropores), is obtained. This is a prerequisite for use of activated carbon foam in areas of application requiring presence of pores of different size.

Fig. 2. SEM images of the carbon foams before (left) and after (right) activation

Conclusions. The obtained results show that the chosen novel approach for increasing the content of micro- and mesopores of the carbon foam samples synthesized by the new method is successful. Activation with water vapour at a high temperature leads to a significant increase in surface area and pore volume, especially micropore volume. The reason for this is the relatively high reactivity of the samples obtained by treatment of the raw material with nitric acid and subsequent carbonization up to 600 °C.

High compressive strength materials were synthesized after heat treatment up to 1000 °C.

The high surface area and well developed porous structure, containing all types of pores will significantly expand the range of possibilities for application of synthesized carbon foam as construction material, purification equipment and medicine.

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*Institute of Organic Chemistry
with Centre of Phytochemistry
Bulgarian Academy of Sciences
Akad. G. Bonchev St, Bl. 9
1113 Sofia, Bulgaria*

*e-mail: Ivanka.Stoycheva@orgchm.bas.bg
Boyko.Tsyntsarski@orgchm.bas.bg
Angelina.Kosateva@orgchm.bas.bg
Bilyana.Petrova@orgchm.bas.bg
Georgi.Georgiev@orgchm.bas.bg
Kalina.Miteva@orgchm.bas.bg*