

## CHEMMOTOGY AND CHEMICAL TECHNOLOGY

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Ihor Voitko<sup>1</sup>,  
Alina Svysch<sup>2</sup>,  
Vasyl Denysovych<sup>3</sup>

### USE OF NATURAL AND SYNTHETIC POLYMERS IN THE PRODUCTION OF CARBON SORBENTS

<sup>1,2</sup>National Aviation University

1, Kosmonavta Komarova Ave., Kyiv, 03680, Ukraine

<sup>3</sup>Institute of Sorption and Problems of Endoecology, 13 Heneralna Naumova, 03164, Kyiv, Ukraine

E-mail: <sup>1</sup>kafedra\_hht@ukr.net; <sup>2</sup>alinasvysch@gmail.com; <sup>3</sup>romb12@i.ua

#### Abstract

**The main purpose** of this article is to find a connection between the experimental physical and chemical properties obtained and sorption characteristics from other polymeric raw materials and products of their processing on carbon adsorbents. **Methods of definition** which were used in the work are the specific bulk mass, the content of volatile substances and ash content, the construction of isotherms of sorption and the calculation of the internal specific surface of methylene blue. **Results:** adsorbents derived from raw materials with a low specific bulk density and high ash content are shown to have relatively low values of the specific internal surface and sorption capacity. The increased content of volatile substances in raw materials and carbonates contributes to the enhanced formation of sorption pores in activated materials. **Discussion:** choosing a polymeric raw material for the production of carbon sorbents it is necessary in addition to other criteria to take into account its physical and chemical characteristics.

**Keywords:** carbon adsorbents; physical and chemical and sorption tests; polymer raw materials; production; recommendations for use

#### 1. Introduction

Carbon adsorbents occupy the leading place, which are used in many industries, including medicine. A variety of materials are used for their production, but natural (bio-) and some synthetic polymers are used to obtain the most effective and clean drugs. For their conversion into the target product, two important technological steps are used, namely carbonization (pyrolysis) and activation [1, 2]. The flow of these processes, as well as the quality of the adsorbents produced, depends on the nature and physical and chemical characteristics of the starting polymers.

Therefore, it was useful to establish a relationship between the type of raw material and the quality of its carbonates and activates. The latter was

determined by the size of the sorption capacity and the specific internal surface.

#### 2. Analysis of the research and publications.

Carbonization is a thermal destruction of the original polymer in order to remove from it non-carbon elements - oxygen, hydrogen, nitrogen, sulfur, creation of the primary porous structure with the provision of strong properties of the product. Chemistry of carbonization of natural polymeric raw materials on an example of fruit stones and shells of nuts are proposed in the literature [3]. Carbonization in this case consists of the following steps:

- in the temperature range 150-350°C there is a decomposition of the least thermostable compounds –

pentosans, with the release in the gas phase of water, oxygen-containing gases, formic and acetic acids;

- at temperatures 325-375°C the decay of cellulose and lignins with the release of water, carbon dioxide, methanol and phenolic products runs;

- with an increase of temperature up to 650°C, complex pyrolytic reactions begin with the formation of active radicals and low molecular weight fragments. At the same time, secondary reactions of recombination (polymerization and polycondensation) occur, which lead to the formation of a semicoke;

- in the temperature range 650-800°C carbonization of the material continues with the formation of coke; the carbon content in the material reaches 85%.

As for polymers of artificial origin, they are divided into two groups [4]: those that are practically non-carbonizable (for example, polystyrene, polyethylene), and therefore have no interest in the production of sorbents and those that can be carbonized (for example, polyacrylonitrile )

The pyrolysis schemes in these cases are quite complex and individual for each of the polymers. For some of them, it is described in [5].

The essence of activation is that the carbonate is heat treated in the presence of some reagents, resulting in a lot of additional pores, cracks and cracks, respectively, repeatedly increases the internal specific surface.

When activated by oxidizing gases (water vapor, carbon dioxide, air), part of the carbon is burned out and removed with lethal compounds and the internal surface increases [6].

### 3. Main material

#### 3.1. Materials and methods which were used in the work

For testing, raw materials such as vinyl styrene resin, sunflower husk and coconut shell, as well as carbonates and activated, obtained from them were taken.

The content of volatile substances, mainly water, was determined by the weight loss of the substance after its exposure to the drying cabinet at a temperature of 120°C for 2 hours.

The content of volatile substances  $w$  was calculated by the formula (1):

$$w = \frac{\Delta m \cdot 100}{m_1}, \% \quad (1)$$

where:

$\Delta m$  - reduction of mass after drying, g;

$m_1$  - initial mass of sample, g

The content of the mineral residue (ash content) in the raw material and its conversion products was determined by weighting in a porcelain crucible in an electric muffle furnace at a temperature of 600-625 °C for 1 hour [7].

Ash content  $z$  is calculated by the formula (2):

$$z = \frac{m \cdot 100}{m_2}, \% \quad (2)$$

where:

$m$  - the mass of the ash residue, g;

$m_2$  - weight loss of the dried sample , g.

Under the volume (bulk density) is understood the mass of material that fills the unit volume under the action of its own weight after shaking.

This value was calculated by the formula (3):

$$\rho = \frac{m}{V}, g / cm^3 \quad (3)$$

where:

$m$  - mass of free matter, g;

$V$  - volume of the filled part of the measuring cylinder,  $cm^3$ .

A method of constructing isotherms of sorption of methylene blue was used to determine the sorption capacity of the samples [9]. To do this, weed 0,0150 g in 8 test tubes, which was added to 10.0  $cm^3$  of solution with increasing concentration of methylene blue from 0 to 2.4 mg/cm<sup>3</sup>. The test tubes were placed in an Orbital Shaker OS20 mixing machine and their contents were shaken for about 6 hours to establish adsorption equilibrium. Then, on the photoelectrocalorimeter KFK-UHLN2 at a wavelength of 440 nm and a thickness of 1,080 mm, the residual concentration of methylene blue was determined and the sorption capacity  $A$  calculated according to the formula (4):

$$A = \frac{(C_0 - C_{eq}) \cdot V}{m} \quad (4)$$

where:

$C_0$  - initial concentration, mg/cm<sup>3</sup>;

$C_{eq}$  - equilibrium concentration, mg/cm<sup>3</sup>;

$V$  - volume of solution, cm<sup>3</sup>;

$m$  - weight of weight of matter, g.

According to these data, sorption isotherms were constructed, which represent a graphical dependence of the sorption capacity  $A$  on the equilibrium concentration  $C_{eq}$ .

Using the data of sorption tests, a specific internal surface was calculated [8].

The molecule of methylene blue ( $C_{16}H_{18}ClN_3S$ ) is adsorbed in a plane orientation relative to the surface and the area of the molecule in this orientation is 1.2 nm<sup>2</sup>. Taking into account the two-layer state of methylene blue on the surface of the adsorbent and the magnitude of its molecular weight (319.85 a.om.), the specific internal surface of the samples was calculated by the formula (5):

$$S_{mc} = \frac{A \cdot N_A \cdot S_m}{M_{mc} \cdot N \cdot 10^{21}}, m^2 / g \quad (5)$$

where:

$A$  - maximum sorption capacity of the sample for methylene blue, mg/g;

$N_A$  - Avogadro number, mol<sup>-1</sup>;

$S_m$  - area occupied by one molecule after adsorption, m<sup>2</sup>;

$M_{mc}$  - molecular mass of methylene blue, g/mol;

$N$  - the number of molecules in the gap, that is, in this case, 2.

The value of the specific internal surface determined by the described method is considerably inferior to the value determined by the BET method [9-10]. This is due to the smaller size of the nitrogen molecules used in the BET method, which may occupy the sorption sites, the next for methylene blue molecules [11].

### 3.2. Experiment results and discussion

Summary data for determining some physical characteristics of the samples under study are given in the table 1.

Table 1

The summary table of physical and chemical characteristics of samples

Sample/ Characteristic	Butadiene-styrene rubber		
	Raw material	Carbohi- zate	Activate
Bulk density, g/cm <sup>3</sup>	0.59	0.42	0.34
Volatile matter content, %	24.60	1.14	1.88
Ash content, %	1.24	1.23	1.79
Sample/ Characteristic	Sunflower seedlings		
	Raw material	Carbohi- zate	Activate
Bulk density, g/cm <sup>3</sup>	0.30	0.10	0.09
Volatile matter content, %	6.67	7.32	7.56
Ash content, %	2.24	8.11	10.14
Sample/ Characteristic	Coconut shell		
	Raw material	Carbohi- zate	Activate
Bulk density, g/cm <sup>3</sup>	0.48	0.59	0.22
Volatile matter content, %	8.77	6.30	0.94
Ash content, %	0.28	0.10	1.10

From the given data, it is clear that sunflower husk has the worst characteristics of bulk density and ash content. Therefore, obviously, they will have the lowest values of the sorption capacity. For samples made of vinyl styrene resin and coconut shells, these characteristics are relatively similar and will have, apparently, a relatively equal sorption capacity.

These assumptions were confirmed by the data of sorption tests presented in the form of isotherms of sorption (fig. 1, 2, 3).

Fig. 1. Isotherms of sorption of carbonizate (1) and activate (2) of coconut shell on methylene blue

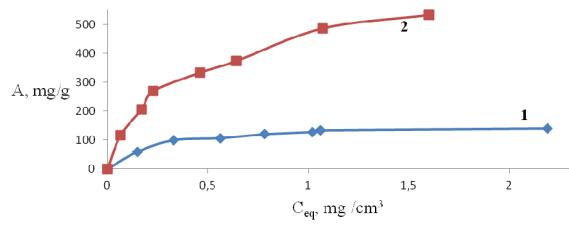
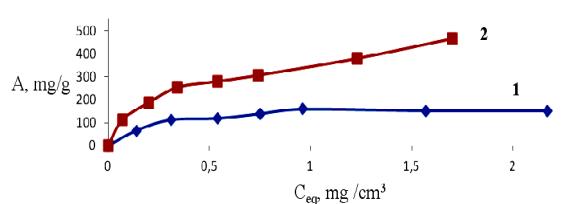
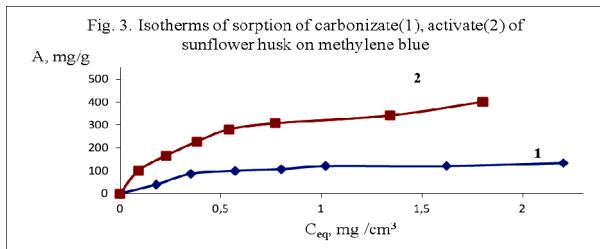


Fig. 2. Isotherms of sorption of carbonizate (1) and activate (2) of butadiene-styrene rubber on methylene blue





The same conclusions can be drawn by analyzing the data presented in the table 2.

Table 2

**The values of the maximum sorption capacity ( $A_{max}$ ) and the specific internal surface of methylene blue ( $S_{ms}$ ).**

Polymer raw materials	Processing products	$S_{MS}$ , $m^2/g$	$A_{max}$ (mg/g)
Coconut shell	Carbonizate	158,2	140,1
	Activate	603,8	533,4
Butadiene-styrene rubber (SCS)	Carbonizate	180,8	153,4
	Activate	527,6	466,9
Sunflower seedlings	Carbonizate	150,3	133,4
	Activate	451,9	400,2

#### 4. Conclusion

From the comparison of experimentally obtained physico-chemical and structural-sorption characteristics of three types of polymeric raw materials and carbonates and activates from them, the following conclusions can be drawn:

- Sorbents, obtained from raw materials with a small bulk density, have low sorption capacities.
- The same dependence is observed in reverse order between the ash content of the initial polymer and the sorption activity of the carbonates and activates.
- The high content of volatile substances, in particular water, in the raw material contributes
  - to the formation of primary cavities in carbonates and sorption pores in activates.

Consequently, when choosing a polymeric raw material for the production of carbon adsorbents, it should, in addition to other criteria, be oriented on its physical and chemical characteristics.

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**I.I. Войтко<sup>1</sup>, А.М. Свищ<sup>2</sup>, В.О. Денисович<sup>3</sup>****Використання природних і синтетичних полімерів у виробництві вуглецевих сорбентів**<sup>1,2</sup>Національний авіаційний університет, м. Київ, проспект Космонавта Комарова 1, 03680, Україна<sup>3</sup>Інститут сорбції та проблем ендоекології НАН України, м. Київ, вул. Генерала Наумова 13, 03164, Україна.E-mail: <sup>1</sup>kafedra\_hht@ukr.net; <sup>2</sup>alinasvysch@gmail.com; <sup>3</sup>tomb12@i.ua

Мета цієї статті полягає у знаходженні зв'язку між експериментальними одержаними фізико-хімічними властивостями з одного боку, і сорбційними характеристиками, з іншої деяких полімерних сировинних матеріалів та продуктів їх переробки на вуглецеві адсорбенти.

Методи, що використовувались в роботі – це визначення питомої насипної маси, вмісту летких речовин і зольності, побудова ізотерми сорбції і розрахунок внутрішньої питомої поверхні за метиленовим синім. Результати: показано, що адсорбенти, одержані із сировини з малою питомою насипною масою і великими показниками зольності, мають відносно низькі значення питомої внутрішньої поверхні і сорбційної ємності. Підвищений вміст летких речовин у сировині і карбонізатах сприяє посиленому утворенню сорбційних пор в активатах. Обговорення: при виборі полімерної сировини для виробництва вуглецевих сорбентів слід, окрім інших критеріїв зважати на її фізико-хімічні характеристики.

**Ключові слова:** вуглецеві адсорбенти; виробництво; полімерна сировина; рекомендації по застосуванню; фізико-хімічні та сорбційні випробування

**И.И. Войтко<sup>1</sup>, А.Н. Свищ<sup>2</sup>, В.А. Денисович<sup>3</sup>****Использование природных и синтетических полимеров в производстве углеродных сорбентов**<sup>1,2</sup>Национальный авиационный университет, г. Киев, проспект Космонавта Комарова, 1, 03680, Украина<sup>3</sup>Институт сорбции и проблем эндоэкологии НАН Украины, г. Киев, вул. Генерала Наумова 13, 03164, Украина.E-mail: <sup>1</sup>kafedra\_hht@ukr.net; <sup>2</sup>alinasvysch@gmail.com; <sup>3</sup>tomb12@i.ua

Цель этой статьи заключается в нахождении связи между полученными экспериментальными физико-химическими свойствами с одной стороны, и сорбционными характеристиками, с другой некоторых полимерных сырьевых материалов и продуктов их переработки в углеродные адсорбенты. Методы, используемые в работе – это определение удельной насыпной массы, содержания летучих веществ и зольности, построение изотермы сорбции и расчет внутренней удельной поверхности с метиленовым синим. Результаты: показано, что адсорбенты, полученные из сырья с малой удельной насыпной массой и большими показателями зольности, имеют относительно низкие значения удельной внутренней поверхности и сорбционной ёмкости. Повышенное содержание летучих веществ в сырье и карбонизатах способствует усиленному образованию сорбционных пор в активатах. Обсуждение: при выборе полимерного сырья для производства углеродных сорбентов следует, помимо других критериев учитывать ее физико-химические характеристики.

**Ключевые слова:** полимерное сырье; производство; углеродные адсорбенты; физико-химические и сорбционные испытания; рекомендации по применению;

**Voitko Ihor** (1938). Doctor (Candidate) of Chemical Sciences, Associate Professor.

Department of Chemistry and Chemical Technology, National Aviation University.

Education: National Technical University of Ukraine "Kyiv Polytechnic Institute", Kyiv (1960).

Reserch area: study of carbon and silicon-containing sorbents.

E-mail: kafedra\_hht@ukr.net

**Svysch Alina** (1996). Student.

Department of Chemistry and Chemical Technology, National Aviation University.

Education: National Aviation University, Kyiv, Ukraine (2017).

Reserch area: carbon sorbents of polymer origin.

Publications: 1.

E-mail: alinasvysch@gmail.com.

**Denysovych Vasyl** (1943). Doctor (Candidate) of Technical Sciences, Senior Research Officer

Institute of Sorption and Endoeontology, National Academy of Sciences of Ukraine.

Education: D. Mendeleev University of Chemical Technology of Russia (1972).

Reserch area: mineral and carbon sorbents.

Publications: 75.

E-mail: romb12@i.ua.