

# Innovative Application Technology for Challenging Inducers of Disease Resistance in Spring Rape in (Nano) Chips

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## Abstract

The present level of development of agricultural science has led to the emergence of a new method of plant protection, it is based on improving the immune potential of plants using elicitors, but not on the destruction of pathogens using pesticides. We have studied the effect of disease resistance inducers based on chitosan, organic acids and other substances with elicitor activity, being part of (nano) chips of different composition (matrix carrier - modified natural minerals, activated carbons, nanotubes, graphene, etc..) for pre-sowing seed treatment and for foliar fertilizing. Active carbons obtained by recycling annually renewable plant wastes (the straw of various oilseed brassica crops), represent a black powder. Powdered activated carbons derived from rape, winter cress, mustard and radish straw according to the developed method (the product yield level is from 5,7% to 17,9%) have the following characteristics:  $A^c$  - 16,5% wt. to 26,2% wt.;  $\Delta$  - from 60,9 g/dm<sup>3</sup> and 140 g/dm<sup>3</sup>; a total pore volume  $V\Sigma$  - from 2,28 to 4,14 cm<sup>3</sup>/g; limiting amount of sorption space  $W_s$  - 0,20 cm<sup>3</sup>/g to 0,69 cm<sup>3</sup>/g; they have an adsorption ability for iodine from 31,0% to 62,0%, for methylene blue - from 64,0 mg/g to 87,0 mg/g. We have studied their influence on growth, development, the incidence of rape plants, the quantity and quality of their crop. We have also determined the efficiency of (nano) chips depending upon their nature and carrier matrix composition. Besides, when using (nano) chips with nanotubes applied as matrix carriers, the yield increase was 14,4-74,0%, depending on their structure; with graphene it was - 22,0%; with active carbons obtained by rape and camelina straw processing, and with Agrosorb, it was - 16,1%; 55,8%; 49,2%, respectively; with mineral derivatives - 5,7-14,8%, depending on their composition; with water-soluble polymers it amounted to 8,0-12,0%, depending on their nature.

Keywords: elicitors, (nano) chips, pre-sowing seed treatment; growth, development, the incidence of rape plants, the quantity and quality of their crop

## Introduction

The present level of development of science has led to the emergence of a new method of plant protection, which is based on enhancing the immune capacity of the plant, rather than on the destruction of pathogens, as is the case with pesticides. Substances that induce protective responses in plants are called elicitors (inducers of disease resistance). The first biogenic elicitor was obtained in 1968, since then their number has been annually growing. Biogenic elicitors are usually used in very small quantities. Plants are "vaccinated" against the disease, which results in their increased disease resistance (Heng, 2010). Such preparations are made both abroad and in Russia, they are produced on the basis of bacterial cultures - «Agat-25K», «Fito-sporin», «Ekstrasol», «Alirin», «Gamair»; some are based on chitosan - «Hitozar», «Narcissus», «Fito-hit», «Agrokhit», «Ekogel»; and some are based on organic acids - «Immunotsitofit», «Obereg»,

«Novosil» (Silk), «Zircon», «Succinic Acid» et al.

The aim of our studies is to investigate the effect of different composition of environmentally friendly (nano) chips based on multi-component poly-functional (nano) systems, including high-sorption-capacity carrier - matrices of different nature (water-soluble derivatives of natural polymers, natural minerals, carbonaceous sorbents, biogenic elicitors - inducers of natural disease resistance (based on chitosan, organic acids and bacterial cultures), as well as the effect of other means of plant protection, their growth and development regulation, used for pre-sowing seed treatment and for the processing of plants during their vegetation with the help of nanotechnology, on the growth, development, yield and quality of rapeseed.

## Methodology

Development and obtainment of new sorption - capacity (nano) chips for pre-sowing treatment,

Tab. 1. General characteristics of the series of carbon nanomaterials CNM: "Taunit", "Taunit-M", "Taunit-MD"

Tab. 1. Ogólna charakterystyka nanomateriałów węglowych CNM: "Taunit", "Taunit-M", "Taunit-MD"

Parameters	"Taunit"	"Taunit-M"	"Taunit-MD"
External diameter, nm	20÷70	30-80	8-15
Inner diameter, nm	5÷10	10-20	4-8
Length, $\mu\text{m}$	2 and more	2 and more	2 and more
Total admixtures, % (after purification)	Up to 5 (up to 1)	Up to 5 (up to 1)	Up to 5 (up to 1)
Apparent density, $\text{g}/\text{cm}^3$	0,4÷0,6	0,03-0,05	0,03-0,05
Specific geometric surface area, $\text{m}^2/\text{g}$	120÷130 and more	180-120	300-320 and more
Thermostability, $^{\circ}\text{C}$	to 600	to 600	to 600

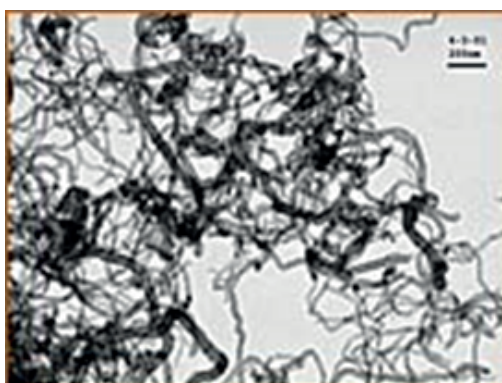


Fig. 1. Electron micrographs based on material "Taunit"

Rys. 1. Obraz mikroskoowy materiału "Taunit"

based on carbon-containing (nano) materials (carbon nanotubes, graphene, activated carbons), silicon dioxide, water soluble polymer and mineral derivatives, as well as the other sorbents together with different plant protection means of biogenic nature, pesticides with sharply reduced application norms (to model conditions in the case of infected backgrounds) are established according to the (Ruban, 2012).

The field trial was conducted using the common for the Central Chernozem region rape crop cultivation technology (Karpachev, 2008). In the trial variants, where we used for seed treatment environmentally friendly (nano) chips, with the elicitors introduced into their composition, we conducted crop spraying with biopesticides in the phases of 4–6 leaves and budding – flowering. In all the field trials phenological and phytosanitary surveillance and surveys were carried out according to the generally accepted methods, and the recommendations developed. To protect rape crop from weeds and pests it was treated with herbicides and insecticides during the vegetation period.

Carbon nanomaterial (CNM) "Taunit" represents the one-dimensional nanoscale thread-like formations of polycrystalline graphite in the fria-

bleform, resembling powder of black color. CNM granules of micrometer dimensions have the structure of tangled bundles of multi-tubes (MWNT) (Figure 1) (Tkachev, 2013). We have obtained some new types of CNM "Taunit" using various catalysts and production modes: carbon nanotubes "Taunit-M" and "Taunit-MD" having the improved morphological and physico-mechanical properties (Figure 2). The optimal heat treatment of the substances, that preceded catalyst and its composition, provides a few-layered CNM with small diameter variation. Table 1 presents data on various CNM.

Active carbons (RAC) obtained by recycling annually renewable plant wastes (the straw of various oilseed brassica crops), represent a black powder (Mukhin, 2012; Voropaeva, 2014; Mukhin, 2014). Powdered activated carbons derived from rape, winter cress, mustard and radish straw according to the developed method (tables 2, 3) (the product yield level is from 5,7% to 17,9%) have the following characteristics:  $A^c$  – 16,5% wt. to 26,2% wt. ;  $\Delta$  – from 60,9  $\text{g}/\text{dm}^3$  and 140  $\text{g}/\text{dm}^3$ ; a total pore volume  $V_{\Sigma}$  – from 2,28 to 4,14  $\text{cm}^3/\text{g}$ ; limiting amount of sorption space  $W_s$  – 0,20  $\text{cm}^3/\text{g}$  to 0,69  $\text{cm}^3/\text{g}$ ; they have an adsorption

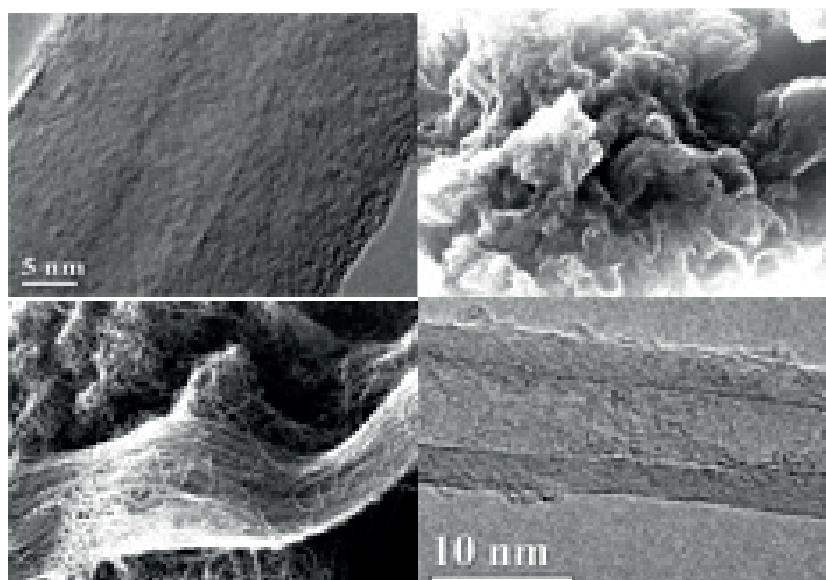


Fig. 2. Electron micrographs of the materials basid on "Taunit-M", "Taunit-MD" with different resolution  
Rys. 2. Obrazy mikroskopowy materiału na baize "Taunit-M", "Taunit-MD"

Tab. 2. General characteristics of the RAC series of active carbons obtained from the straw of oilseed brassica crops: "RAC-rape", "RAC-winter cress", "RAC-mustard", "RAC-false flax", "RAU-radish"

Tab. 2. Charakterystyka serii węgla aktywnych RAC otrzymanych ze słomy roślin oleistych "RAC-rape", "RAC-winter cress", "RAC-mustard", "RAC-false flax", "RAU-radish"

Sample	$V_{\Sigma}$ , cm <sup>3</sup> /g	$W_{ss}$ , cm <sup>3</sup> /g	Moisture, %	$\Delta$ , g/dm <sup>3</sup>	Total, %	Sorption capacity with:		Total ash, %	Output the volatile, %
						iodine, %	Methylene- blue MG, mg/g		
1. Rape	4,14	0,48	2,4	135	10,3	39	87	16,5	16,0
2. Falseflax	2,43	0,69	5,7	140	5,7	43	82	15,6	12,6
3. Radish	2,55	0,20	2,2	131	17,9	31	69	26,2	15,3
4. Wintercress	2,28	0,57	1,5	135	8,1	62	73	22,1	12,8
5. Whitemustard	4,0	0,45	2,8	60,9	11,0	50	64	24,4	11,2
6. Brownmustard	2,81	0,57	3,4	111	7,3	56	67	27,3	10,6

ability for iodine from 31,0% to 62,0%, for methylene blue – from 64,0 mg/g to 87,0 mg/g. Electron micrographs of powdered activated carbon from straw rape, winter cress and mustard are shown in Figure 3.

Thus, well developed total porosity and relatively vast sorption space allow to effectively use the resulting adsorption RAC for those technologies where powdered activated carbons are used.

## Results and discussion

Using new nanomaterials in the agricultural sector to solve various problems of agricultural production is one of the foreground goals of today. The studies conducted at Arkansas University of Nanotechnology Center at Little Rock, also at Tambov State University named after G.R. Derzhavin (Training Innovation Center for Nanotechnologies and Nanomaterials) together with the Tambov State Technical University (Co Ltd "NanoTehTsentr") and others, have shown that putting

Tab. 3. The micropore volume and micropore size for the isotherms of a series of activated carbons RAC obtained from the straw of oilseed brassica crops: "RAU-rape", "RAU-winter cress", "RAU-mustard", "RAU-false flax", "RAU-radish"

Tab. 3. Objętość i wielkość mikroporów dla węgla aktywnych RAC otrzymanych ze słomy roślin oleistych kapusnych: "RAU-rape", "RAU-winter cress", "RAU-mustard", "RAU-false flax", "RAU-radish"

Sample	Micropore volume, cm <sup>3</sup> /g	Equivalent pore width, nm		S <sub>equ</sub> , m <sup>2</sup> /g	E <sub>a</sub> , kilojoule/mole
		average	modal		
<u>oil-bearingcabbageplants</u>					
Rape	0,161	1,58	1,42	454	22,7
Falseflax	0,135	1,66	1,53	380	19,8
Wintercress	0,124	1,53	1,38	350	24,9
Whitemustard	0,161	1,57	1,39	454	23,2
Brownmustard	0,163	1,50	1,32	459	26,2
Radish	0,116	1,62	1,51	328	21,0

tomato seeds, tobacco, sainfoin, rape, wheat and some other crops into a nutrient solution containing carbon nanotubes leads to stimulation of their germination, plant growth and development improvement, biomass accumulation increase and also to higher yields due to the penetration of nanotubes through the seed coats into various plant organs (Gusev, 2014). We have also managed to identify the effects, observed during our experiments, where we used for pre-sowing seed treatment new nano-porous (nano) chips based on carbonaceous sorbents with the different plant protection products of biogenic nature included into their composition.

The conducted laboratory studies have shown that the treatment of rape seeds before sowing using nanoporous carbonaceous materials ("Taunit", "Taunit-M," "Taunit-MD", graphite and activated carbons obtained from the straw of different crops (table 1, 2, 3; fig. 1, 2, 3) with the micronutrient malnutrition included into their composition, as well as the drugs with fungicidal, bactericidal and eliciting properties, tended to sharply accelerate the process of seed germination (the number of "arisen" seeds on the first germination day, depending on the composition, was 20,2–32,5% (while in the control variant (where the seeds have not been treated) it was – 19,8%), on the second day it was 90,5–93,0%. It also facilitated the increase of vigor, laboratory germination, seedling length and fresh weight accumulation, which can be probably explained by the possibility of the idea that physiologically active polyfunctional

(nano) chips based on nanotubes penetrate inside the seed and then into the cells and tissues of seedlings and plants.

The conducted field trials revealed an obvious differentiation between the various trial variants depending on the composition of multifunctional complex (nano) chips applied to the surface of rape seeds in the process of pre-treatment using (nano) technology and in the process of crop spraying with biopesticide having an eliciting activity. Besides, when using (nano) chips with nanotubes applied as matrix carriers, the yield increase was 14,4–74,0%, depending on their structure; with graphene it was – 22,0%; with RAU active carbons obtained by rape and camelina straw processing, and with Agrosorb, it was – 16,1%; 55,8%; 49,2%, respectively; with mineral derivatives – 5,7–14,8%, depending on their composition; with water-soluble polymers it amounted to 8,0–12,0%, depending on their nature.

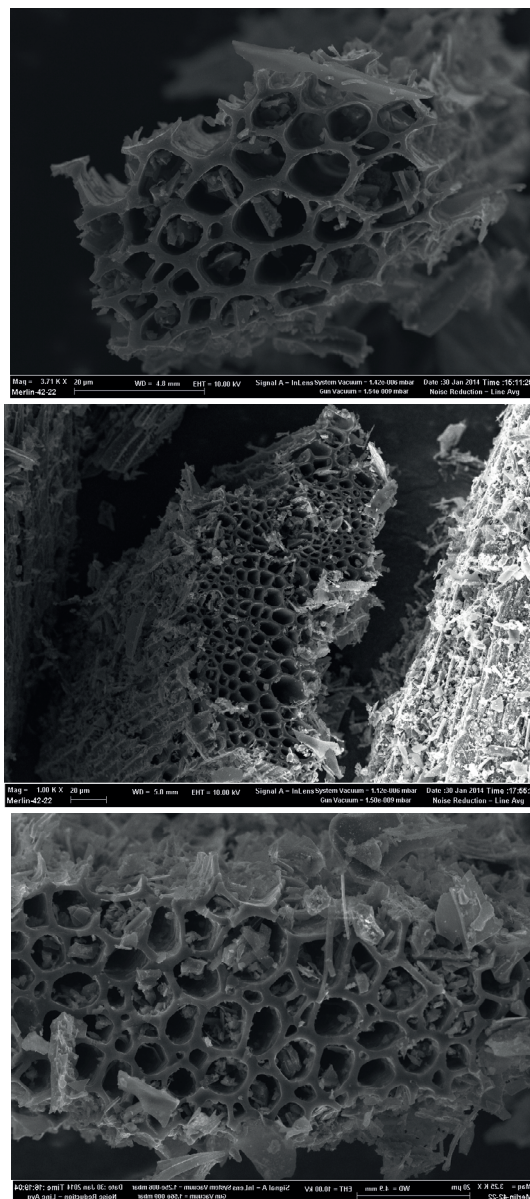
## Conclusion

Thus, when applying a nanotechnology while processing the surfaces of seeds and plants, nano-sized structures are being formed, providing a high efficiency of mineral nutrition process, plant protection and development, and also contributing to the following yield increase. In connection with the stated above, sorption-capable nanoporous materials can be effectively used to transfer the preparations with elicitor activity, to transfer the necessary plant protection products and their trace elements to accelerate seed ger-



Fig. 3. Electron micrographs of powdered activated carbon, obtained from rape straw – 1, mustard straw – 2, winter cress straw – 3

Rys. 3. Obraz mikroskopowy sproszkowanego węgla aktywnego uzyskanego ze słomy rzepakowej – 1, rzeżucha biała słomy – 2, słóma rzeżuchy zimowej – 3



mination process, to improve plant growth and development.

#### Acknowledgements

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"Create a new oilseed varieties of cabbage crops, combining high productivity with resistance to major pathogens, pests, abiotic stressors, technological in production" and the assignment № 16.711.2014/K to perform a research under the project of the state task to the educational organizations and higher education scientific organizations under RF Ministry of Education and Science.

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### *Innowacyjna technologia wskaźników odporności na choroby w Spring Rape w (Nano) Chips*

Obecny poziom rozwoju rolnictwa pozwolił na odkrycie nowej metody ochrony roślin. W tej metodzie wykorzystuje się elicytory mające poprawić potencjał immunologiczny roślin, zamiast niszczyć patogeny z użyciem pestycydów. Zbadano wpływ induktorów odporności na podstawie chitozanu, kwasów organicznych oraz innych substancji wykazujących aktywność elicytacyjną, będących częścią (nano) wiórów o różnym składzie (nośniki – modyfikowane minerały naturalne, węgle aktywowane, nanorurki, grafeny itp.) na przygotowanie przedsiwne ziarna i na nawożenie dolistne. Węgla aktywne otrzymane z całorocznego recyklingu odnawialnych odpadów roślinnych (słoma z różnych rodzajów roślin oleistych z gatunku brassica). Sproszkowane węgle aktywowane otrzymane z rzepy, zimowej odmiany rzeżuchy, słomy z gorczycy i rzodkiewki wg opracowanej metody (wydajność produktu sięga od 5,7% do 17,9%), posiadały następujące właściwości:  $A^c$  – 16,5% wagi procentowej to 26,2% wagi procentowej;  $\Delta$  – od 60,9 g/dm<sup>3</sup> i 140 g/dm<sup>3</sup>; całkowita ilość porów  $V\Sigma$  – od 2,28 do 4,14 cm<sup>3</sup>/g; ograniczająca wartość powierzchni sorpcji  $W_s$  – 0,20 cm<sup>3</sup>/g do 0,69 cm<sup>3</sup>/g; ze zdolnością adsorpcji dla jodu od 31,0% do 62,0%, dla błękitu metylenowego – od 64,0 mg/g do 87,0 mg/g. Zbadano ich wpływ na wzrost, rozwój, częstotliwość upraw roślin rzepakowych, ilość i jakość upraw. Określono również wydajność (nano) wiórów w odniesieniu do ich składu naturalnego i w nośniku. Ponadto, przy użyciu (nano) wiórów z nanorurkami użytymi jako nośnik, wzrost wydajności wyniósł 14,4–74%, w zależności od ich budowy; przy grafenie wzrost wyniósł 22,0%; z węglami aktywnymi otrzymanymi z przetwarzania rzepy i lnicznika siewnego, wraz z Agro-sorbem, wzrost wydajności wyniósł odpowiednio 16,1%; 55,8%; 49,2%; z derywatami mineralnymi – 5,7–14,8%, w zależności od ich składu; z polimerami rozpuszczalnymi w wodzie wzrost był rzędu 8,0–12,0%, w zależności od ich charakteru.

Słowa kluczowe: nano czipy, zaprawianie nasion przed siewem, wzrost, rozwój, występowanie roślin rzepaku, ilość i jakość ich uprawy