RECLAMATION OF PLANT WASTES (STRAW) AND OBTAINING (NANO) CHIPS WITH BACTERICIDAL PROPERTIES BASED ON THEM

Dedicated to the bright memory of professor I. N. Ruban.

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Abstract

Rape, camelina, wheat and Jerusalem artichoke vegetable wastes (straw) as annually renewable raw materials were processed into activated carbons, which were modified with silver nanoparticles for carbonaceous sorbents to acquire specific properties, since carbonaceous sorbents are usually widely used in the food industry, agriculture, medicine and other fields of human activity. The technology to obtain active carbons from agricultural crop residues has been developed, active carbon physico-chemical and adsorption properties, textural characteristics have been studied, new functional carbon (nano) materials with antibacterial activity containing (nano) particles of silver have been obtained, their influence within (nano) chip composition on rape crop growth, development and yield has been studied. In the conducted field tests, the highest activity was noted when using the (nano) chip whose structure included RAC - camelina and silver nanoparticles. Besides, when nano chips are used for seed treatment, the yield increase makes up 11.6 % for nanoparticles containing Ag, for plant active carbons (PAC) (rape) with Ag this index makes up 28.1 %, for RAC (Camelina) with Ag it makes up 55.8 % (compared to the control variant), which can be explained by the differences in the sorption characteristics of the studied radio activated carbons. Our results and the previous studies of other authors can prove the fact that silver nanoparticles (including those being a part of (nano) chips) "get" into the biochemical processes and have a pronounced phytostimulating effect on plants, which was especially obvious when suppressing the activity of plant pathogenic microflora by silver nanoparticles.

Keywords: active carbons, (nano) particles of silver, new functional (nano) materials, vegetable agricultural wastes, processing technology.

Introduction

One way to create functional materials with the desired properties and the specific functional activity is to introduce metal nanoparticles (NPs) into their structure. Creating nanocomposite materials based on metal nano-sized particles and semiconductors is currently an urgent task due to their possible application in various fields of science and technology. Therefore, the solution of actual problems of modern nanochemistry is closely related not only to the further development and improvement of synthesis methods, nanoscale structures stabilization, but also to the creation of nanocomposite materials with the desired properties and functional activity based on them.

One way to solve the problem of synthesis of stable nano-sized particles in the liquid phase through the "molecular assembly" method is to use reverse micelles as micro reactors. In such systems, the aggregation of nanoparticles decreases in the presence of surfactants [1, 2].

In the age of (nano) industry, a specific role in the agricultural sector is played by the innovative drugs for crop production based on the new (nano) materials [1-8]. In particular, the influence of colloidal silver and a variety of (nano) systems based on it (for example, modified by polyhexamethylene biguanide hydrochloride) on the growth and development of various crops (oilseed rape, ryegrass, barley, flax, etc.) has been studied [4,8]. Besides, it has been determined that 0.0015 % colloidal silver has the maximum efficiency. The composition of materials has been patented, including metallic silver nanoparticles, silver alloys with antimicrobial properties, where metallic nanoparticles are put or encapsulated into the matrix of chitosan and its derivatives [5]. In [6] our work, we carried out a modification of chitosan lactate (the main active ingredient of Ekogel preparation, which acts as an inducer of the immune system, having certain fungicidal properties) with Ag ions with the magnetic structuring of the solution. In this innovation [7], as a source of silver nanoparticles, we used colloid solution AgBion-2 with the concentration of 0.0047 %, and the application rate was 10 L/tonne of seeds.

It has been shown that all the studied materials have certain biological activity, significantly stimulating the development of seedlings (increasing sprout and root length), besides, they contribute to the anti-stress resistance in plants under adverse environmental conditions, including after the treatment with pesticides. The preparations are introduced on the surface of the seeds before planting and during the growing season, which allows to accelerate the growth and development of crops, to reduce the growing season, particularly in the areas of risk farming, and it also helps to increase crop productivity.

In our research [4, 8], we successfully assessed the environmental toxicity of three types of silver nanoparticles ranging in size from 1 to 20 nm with the concentration of 0-100 mg/L during germination of seeds on ryegrass, barley and flax plant areas. The germination was carried out using both the soil and the sand. It was found that certain inhibition of the germination process began with the silver nanoparticle concentration of 10 mg/L, but the complete suppression has not been achieved. A sprout length indices change proved to be a more sensitive indicator of ecotoxicity, not the germination. The size of the silver nanoparticles had no significant effect on their toxicity. Soil type only slightly affected the ecotoxicity indices.

The aim of our studies consists in developing the surface modification methods for coal using natural raw materials to study the physic-chemical properties and bactericidal activity of the obtained preparations on the basis of Ag NP for pre-sowing rapeseed and other oilseeds treatment.

Materials and methods

Before sowing, rapeseeds has been treated according to the seeing material preparation nanotechnology with the help of (nano) chips, they have also been tested for germination energy and germination capacity using Petri dishes and a filter paper according to State standard N 12038-84 "Seeds of agricultural crops: methods for the determination of germination"[9, 10]. In addition, we determined the linear sizes and weight of the aerial and underground parts during the development of plants. As the control variant, we used the seeds with no treatment at all. The seeds and seedlings were regularly irrigated with distilled water. The specific tested concentrations were selected on the basis of existing literature data and the results of our previous experiments [9, 11-13]. The pre-sowing rapeseed field test was performed according to the patent [9]. The field experiment was conducted in accordance with the procedure common for rape crop cultivation in the Black Earth region of Russia [14]. When using environmentally friendly (nano) chips for the treatment of seeds with the introduced elicitors and silver nanoparticles, we also carried out spraying the plants with biopesticides in the phases of 4-6 leaves and budding - flowering. In all the field trials, we carried out phenological, phytosanitary monitoring and accounting in accordance with the generally accepted methods and developed recommendations.

As carrier matrixes in (nano) chips, we used the activated carbons that we had developed (RAC) from annually renewable primary plant wastes – rapeseed straw and stalks (specific gravity d = 135 g/dm3), false flax (d = 140 g/dm^3), wheat (d =137 g/dm^3), Jerusalem artichoke (d – 95.3 g/dm^3) [15]. The coal samples were prepared from the plant wastes (straw): "artichoke"(I), "false flax" (II), "wheat" (III) and "rape"(IV).

Silver nanoparticles (Ag NPs) were prepared according to the procedures described in the following works [16-18]. The synthesis of silver nanoparticles is based on the recovery of metal ions in the reverse micellar solutions (Fig. 1).

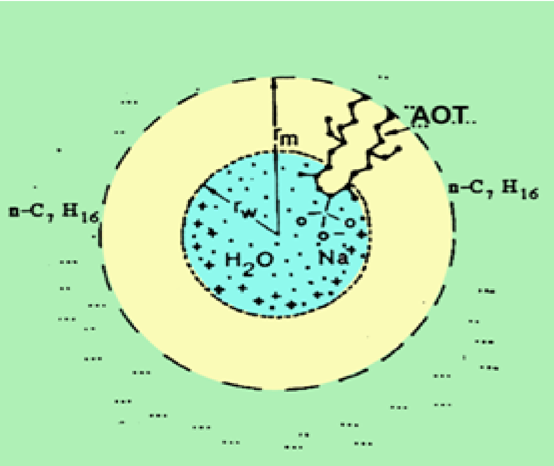

Fig.1. Scheme of reverse micelle

In this study, we have chosen two methods of synthesis of silver nanoparticles: the radiation-chemical (RadChem) and chemical (Chem) recovery of ions and the formation of nanostructures (by a "molecular assembly" method) in the reverse micellar solutions. The main difference between these two methods consists in that the RadChem synthesis is carried out under anaerobic conditions, and the Chem synthesis is carried out necessarily in the presence of oxygen and flavonoids, as a catalyst.

In the method of radiochemical synthesis, the main reducing agents can be electrons and other restorative particles which are formed by ionizing radiation in aqueous-organic systems. In the method of chemical synthesis [17, 18], quercetin can be used as a reducing agent, quercetin (3, 3', 4', 5, 7 – pentahydroxyflavone) – a natural pigment from the group of flavonoids with antioxidant, immune stimulating, bactericidal properties [19]. Besides, the recovery takes place only in the presence of oxygen, which plays an important role in the synthesis reaction. The structural formula of quercetin is shown in Fig. 2.

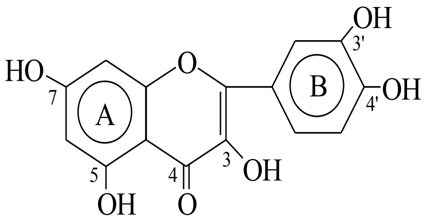

Fig.2 The structural formula of quercetin (3, 3 ', 4', 5, 7 - pentagidroksiflavon).

In reverse micellar solutions of metal nanoparticles, one can observe the appearance of specific optical absorption band. For most metals, this band is in the near-ultraviolet spectral region, but for three metals - Ag, Au and Cu - it is in the visible region of the spectrum. For silver nanoparticles in reverse micellar solutions of H2O/AOT/isooctane, the highest point of this optical absorption band is located in the range of 400-450 nm. To study the NP formation and the silver NP solution concentration change after the contact with the silver surface of the adsorbent (at room temperature), we used the UV-VIS spectrophotometer method (Hitachi U-3310 spectrophotometer). To study the effect of radiation-chemical treatment of coal on Ag NP adsorption, a part of dry samples was exposed to ionizing radiation gamma - 60Co (Dose 20kGr).

We have studied the kinetics of Ag NP formation and evolution from the period of samples storage after the synthesis or modification of their concentration while interacting with other components. The measurements of optical absorption spectra (OA) and luminescence studied solution indices have been taken. Figures 3-4 show OA spectra during the adsorption of silver nanoparticles on the RAC carbonaceous materials. The analysis of the results showed that all of the coals from natural raw materials were good adsorbents, but the nature and kinetics of adsorption was determined by the type of natural resources. Thus, it is of some certain interest to clarify the nature of the active centres responsible for the Ag NP adsorption.

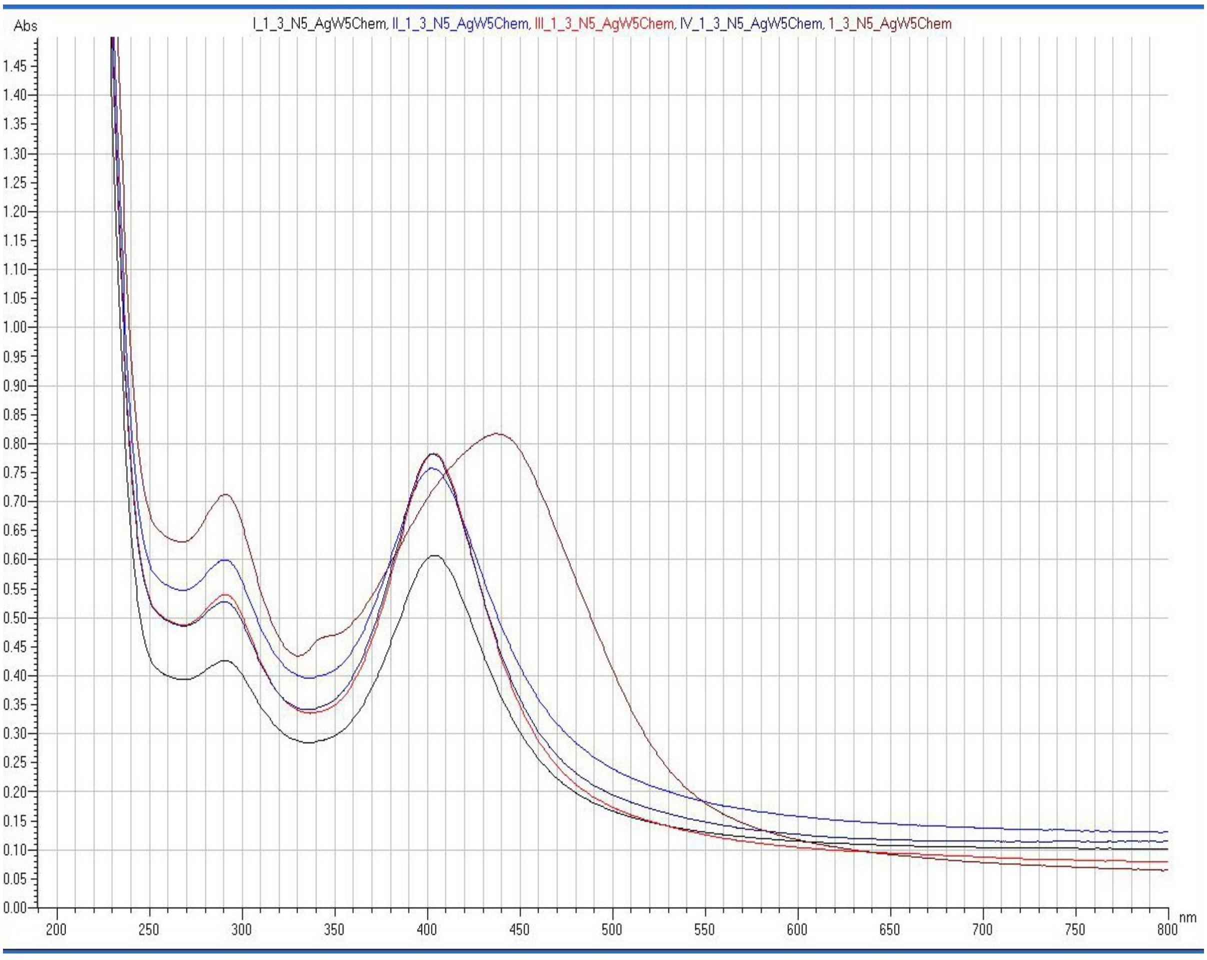

Fig. 3 OA spectra of the initial solution with Ag NP (w-5.0), diluted with isooctane 1:3 (spectrum – Ag w = 5Chem) and their further changes after the contact with different active carbon (AC) samples (artichoke - I, false flax - II whet - III, rape - IV) within 1.5 hours.

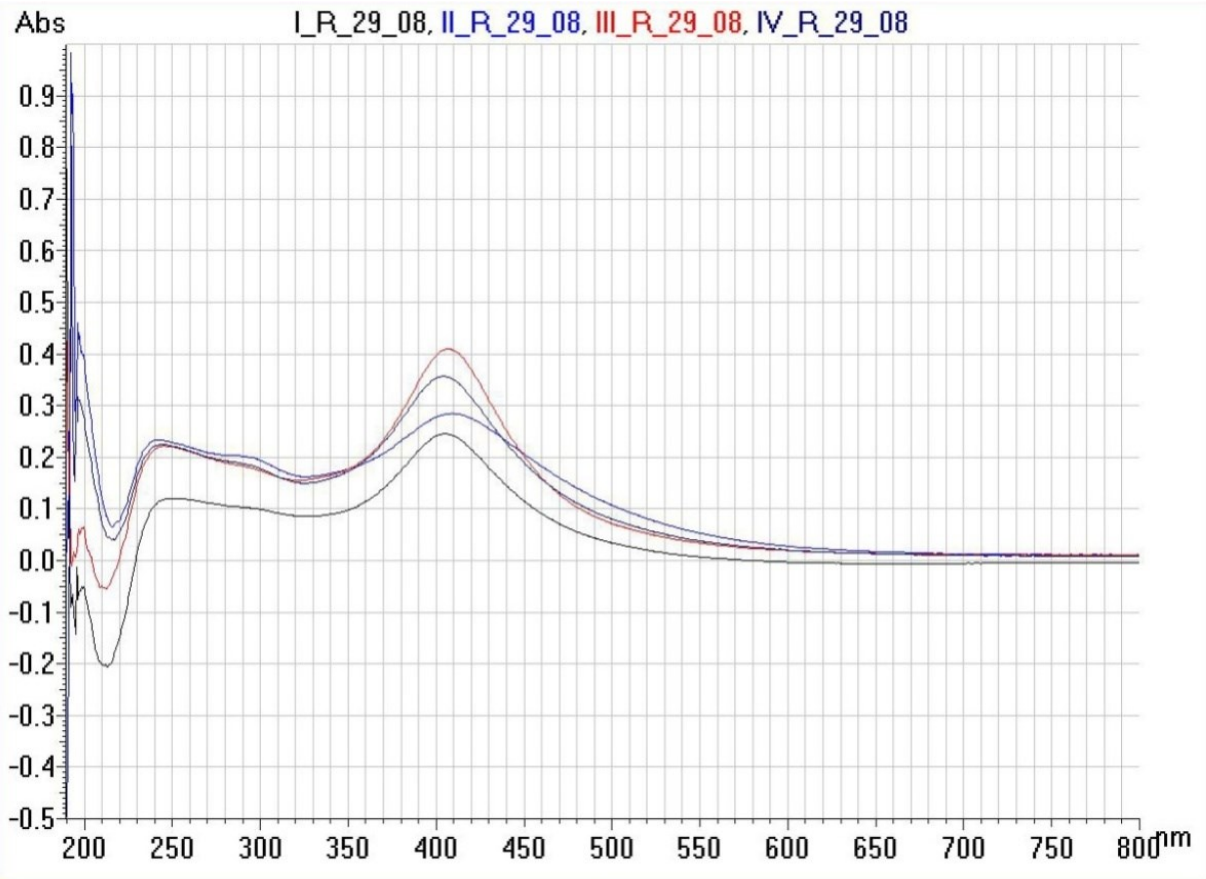

Fig. 4 OA spectra of the solution with Ag NP (w-5.0), diluted with isooctane 1:3 after the contact with different active carbon (AC) samples during 24 hours.

In the initial OA solution with Ag NP (w = 5 of Ag), the concentration of Ag+ was 4 мM; when the solution was diluted 1:3, the index was 1.33 мM. The AC samples with the necessary mark "artichoke"(I), "false flax" (II), "wheat" (III) and "rape"(IV) were placed into the sample bottles, where 3 ml of OA solution with Ag NP were added with the concentration of Ag+ being 1.33 мM. The OA spectra measurements in two days showed the absence of Ag nano particles absorption band.

The study of the physicochemical properties and structural features of coal was carried out using the method of electron paramagnetic resonance (EPR). We used glass vials made of special glass, such as "Luch", which allows them to irradiate coals without any signal distortion. It was found that the ESR source sample signals had characteristic signals near the absorption of the electromagnetic field by free electrons, but they differed in shape and intensity. The change in the coal EPR spectra properties after the exposure to ionizing radiation confirms the feasibility of additional radiation-chemical treatment of raw coal to increase the adsorption capacity of coal in relation to Ag NP and biological activity of natural raw materials.

Results and discussion.

The data obtained as the result of the studies of the biological effects applied to a (nano) chip seed surface, with silver nanoparticles included into the chips, showed that all the investigated (nano) chip contents and silver nanoparticles concentrations affected the growth and development of seedlings, detecting significant differences in roots and stems lengths having a strong stimulant effect. The lengths of the roots and seedlings have been measured on the 3rd and the 5th day according to the general method [4] and the patent [9]. The maximum effect (100 % for a root, 20 % for a stem) is achieved during the seed treatment with the following (nano) chips. The germination capacity and seedling vigour decreased slightly compared to the control variant at its maximum with the following (nano) chips (about 20 %). This may be explained by previously developed action mechanism of coatings, impacting physiological and biochemical processes in the seeds during the germination process which is associated with a decrease in the water flow rate within the treated seeds. In the conducted field tests, the highest activity was noted when using the (nano) chip whose structure included RAC-camelina and silver nanoparticles. Besides, when nano chips are used for seed treatment, the yield increase makes up 11.6 % for nanoparticles containing Ag, for plant active carbons (PAC) (rape) with Ag this index makes up 28.1 %, for RAC (Camelina) with Ag it makes up 55.8 % (in comparison to the control variant), which can be explained by the differences in the sorption characteristics of the studied radio activated carbons.

Our results and the previous studies of other authors can prove the fact that silver nanoparticles (including those being a part of (nano) chips) "get" into the biochemical processes and have a pronounced phytostimulating effect on plants especially obvious when suppressing the activity of plant pathogenic microflora by silver nanoparticles [4,20].

Conclusion

Thus, our studies suggest that (nano) chips we succeeded to develop have certain biological activity, significantly stimulating the growth of wet and dry weight of stems and roots of rape plants. At the same time, the yield increase makes up 11.6-55.8 % depending on the composition of (nano) chips. Taking into consideration the fact that (nano) chip compositions we studied are formed on the basis of RACs which have been derived from annually renewable inexhaustible plant wastes (straw) of rapeseed, camelina, wheat and Jerusalem artichoke (which determines the possibility of their application in industrial scale), and they also have been modified with silver nanoparticles to get specific properties for new carbonaceous (nano) materials for agriculture. It should be noted that they have attractive prospects for their future application in various spheres of human activity. In the sphere of agriculture, they can be recommended for the treatment of seeds and the processing of plants during the growing season.

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