The Effect of Iron Nanoparticles on Physico-Chemical Properties and Functional Activity of Active Carbon from Plant Materials

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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 iron 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.

Keywords: activated carbons, Fe - nanoparticles, functional materials, paramagnetic properties, agricultural crop residues, technology of modification

Introduction

The problem of agricultural plants'protection in the cultivation of various crops, despite the great number of existing forms of preparation for chemical means for plants' protection, have been and remain relevant [1]. Of particular interest here are the new (nano) forms of plant protection products and the regulation of growth processes that combine nanotechnology innovations and advancements of phytosanitary. One of the important applications of nanotechnology approaches in agriculture is to produce nanosized particles of various metals and their use as ultramicroelements having the properties of plant growth stimulants [1–3]. For example, it is shown that nanosized iron promotes seed germination, while fostering the development of the root system of plants [2]. One of the way to create a new nanomaterials with desired properties and biological activity for agriculture, particularly for crop production, is the introduction of metal nanoparticles (NPs) of "vital importance" into different metal matrix carriers to facilitate their retention on the surface of the biological material of plant and extension activities.

Earlier the studies of the effect of silver and other metals nanoparticles on the sowing qualities of spring rape seeds were carried out [4–8]. Also methods for modifying by silver nanoparticles the carbonaceous sorbents surface from natural raw materials were developed. There were studied the physico-chemical properties of new nanoproducts on the base of silver nanoparticles (Ag NPs) and biological activity of new nanocomposites are used at presowing of rape seeds and other oilseeds.

The samples of activated carbons (AC) were prepared from vegetable agricultural waste remaining after harvest of Jerusalem artichoke, camelina, wheat and rape [6–8]. The investigation of AC radiation-chemical treatment was carried out by using spectrophotometry method to estimate the effectiveness of Ag NP adsorption from reverse micellar solutions by activated carbon [7,8]. Analysis of the results showed that all activated carbons from natural vegetable materials are good adsorbents, but the activity and kinetics of adsorption are determined not only by the natural raw material species, as well as temperature and other technological characteristics of methods for producing carbon materials. However it remained unresolved question of the nature of the AC active centers responsible for the metal NP adsorption and the biological activity obtained nanocomposite materials.

In the present study the electron paramagnetic resonance method (EPR) was selected for investigation of the AC reaction centers and the iron nanoparticles effect on their properties. The impact of ionizing radiation of gamma-60Co rays (absorbed dose of 10 ÷ 20 kGy) on dry samples for surface modification of carbon materials.

Materials and Methods

We used the AC received by high-temperature pyrolysis of vegetable carbonaceous feed waste: Jerusalem artichoke, camelina, wheat and rape [9-

Tab. 1. The properties of activated carbons from RAU primary waste vegetable raw materials

Tab. 1. Właściwości węgla aktywnego z biomasy z odpadów organicznych

Sample	V_Σ, cm^3/g	Humidity, %	Δ, g/dm^3	Adsorption of iodine, %
1. Jerusalem artichokes (I)	3,00	1,0	95,3	34
2. Camelina (II)	2,43	5,7	140	43
3. Wheat (III)	3,61	1,9	66,5	64
4. Rape (IV)	4,14	2,4	135	39

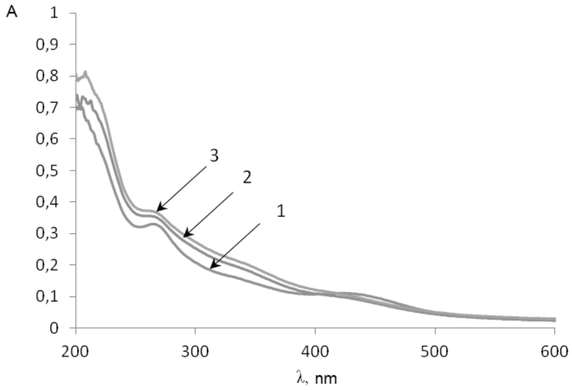

Fig. 1. The optical absorption spectra of the iron NPs (Chem) in 0.15M AOT/isooctane with solubilization coefficient ω=1.5 - 1, ω=3.0 - 2, ω=5.0 - 3 (1 day after the synthesis), the RMS (0.15M AOT/isooctane) was selected as a reference

Rys. 1. Widmo absorpcji optycznej NPs żelaza (Chem) w 0,15 M AOT / izooktanu z współczynnik rozpuszczania T = 1,5 - 1, ω = 3,0 - 2, ω = 5,0 - 3 (1 dzień po syntezie) RMS (0,15M AOT / izooktan) został wybrany jako punkt odniesienia

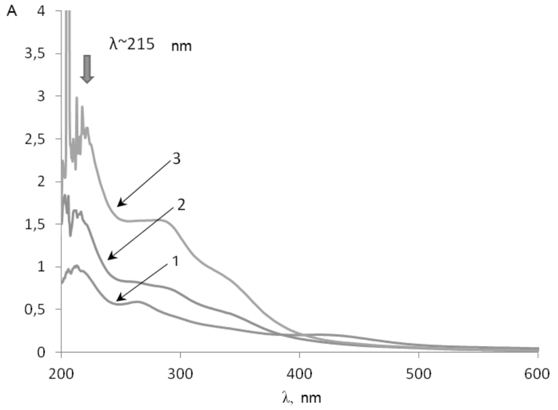

Fig. 2. The optical absorption spectra of the iron NPs (Chem) in 0.15M AOT/isooctane with solubilization coefficient ω=1.5 - 1, ω=3.0 - 2, ω=5.0 - 3 (27 days after the synthesis). Reference - 0.15M AOT/isooctane

Rys. 2. Widmo adsorpcji optycznej NPs żelaza (Chem) w 0,15 M AOT/izooktanu z współczynnikiem rozpuszczania T = 1,5 - 1, ω = 3,0 - 2, ω = 5,0 - 3 (27 dni po syntezie). Ciecz referencyjna - 0,15 M AOT/izooktan

11]. Some properties of these carbon nanomaterials are presented in Table 1

Studies of physicochemical properties AC performed on initial samples, and after grinding and after radiation-chemical treatment of dry state samples. The exposure to ionizing radiation (gamma- 60Co rays) was chosen as a radiation-chemical method for modifying the coal surface. The power of the dose (RHM-γ-20, Mendeleev UCTR), equal to ~ 0.1 kGy*s-1 and a dose in the range of 20 kGy determined using ferrosulfate dosimetry.

For iron NP synthesis were used two methods: the radiation-chemical (RadChem) and chemical (Chem) reduction of metal ions and the formation of nanostructures (by “molecular assembly”) in reverse micellar solutions (RMS). The main difference between these two methods is that RadChem synthesis is carried out under anaerobic conditions, and Chem - necessarily in the presence of oxygen and flavonoid quercetin, as catalyst [12–15].

Formation of iron NP and change of their concentration in the RMS after contact with the AC were detected by UV-VIS Spectrophotometry (spectrophotometer Hitachi U-3310).

Analysis of the results showed that all of the AC based on natural raw material waste are good adsorbents, but the nature and kinetics of adsorption of iron nanoparticles by AC obtained from straw of different crops are different. To study the physicochemical properties and structural features of AC EPR method was used (EPR spectrometer PS 100.X) [11]. AC samples were placed in glass vials made of special glass such as “Luch”, which allowed them to carry out irradiation of samples and registrate only paramagnetic AC particles signals without EPR signal of irradiated glass.

Results and Discussion

Chemical reduction method (Chem). Reduction of metal ions and the Fe NP formation oc-

Tab. 2. The change in absorbance of Fe NPs (at the selected wavelengths) during storage time of the samples, Δt

Tab. 2. Zmiana absorbancji żelaza NPs (dla wybranych długości fal w czasie długiego składowana próbek, Δt

ω_i		λ_1=270 nm			λ_2=350 nm			λ_3=430 nm		
	Δt, days OD	1	8	15	1	8	15	1	8	15
1.5		0.32	0.44	0.50	0.14	0.19	0.20	0.11	0.18	0.20
3.0		0.35	0.46	0.55	0.17	0.22	0.28	0.09	0.09	0.09
5.0		0.36	0.49	0.55	0.19	0.26	0.27	0.10	0.07	0.07

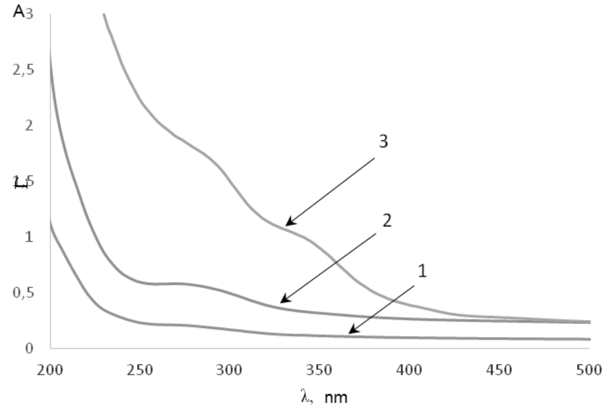

Fig. 3. The optical absorption spectra of the iron NPs (RadChem) in RMS, synthesized using radiation-chemical reduction of metal ions in solutions with solubilization coefficient ω=1.5 - 1, ω=3.0 - 2, ω=5.0 - 3 (27 days after the synthesis). Reference - 0.15M AOT/isooctane

Rys. 3. Widmo absorpcji optycznej NPS żelaza (RadChem) w RMS, syntetyzowano stosując redukcję chemiczną promieniowanie jonów metali w roztworach o współczynniku rozpuszczenia T = 1,5 - 1, ω = 3,0 - 2, ω = 5,0 - 3 (27 dzień po syntezie). Ciech referencyjna - 0,15 M AOT/izooktan

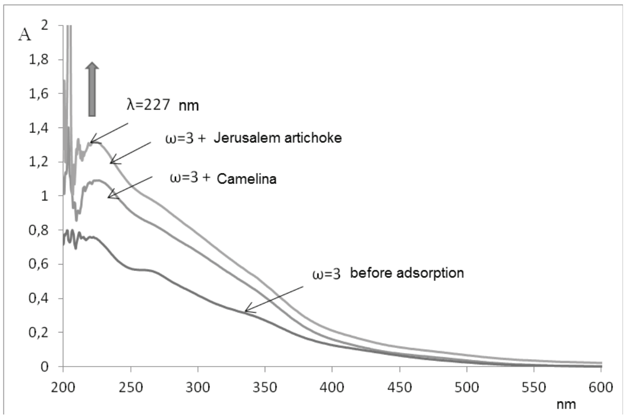

Fig. 4. Fe NP RMS ω=3,0 optical absorption spectra changes after the contact with AC samples obtained from residues of Jerusalem artichokes and Camelina within 3 days. Reference – 0.15M AOT/isooctane

Rys. 4. Fe NP RMS ω = 3,0 optyczne zmiany widma absorpcji po kontakcie z AC próbek uzyskanych z pozostałości topinamburu i lnu w ciągu 3 dni. Ciecz referencyjna - 0,15 M AOT/izooktan

curs in aerated solutions Men+/H2O/0.15M AOT/isooctane in the presence of the natural polyphenol compound flavonoid quercetin (Qr). The concentration of Qr in the 0.15M AOT/ isooctane solution (AOT - bis (2-ethylhexyl) sodium sulfosuccinate) was used 150 µM. The aqueous solution of 0.3M Mohr's salt $((NH_4)2Fe(SO_4)_2*6H_2O)$ was injected into Qr/H_2O/AOT/isooctane solution in accordance with the selected coefficient values of solubilization equal molar ratio ωi: 1.5, 3.0, 5.0. Optical absorption spectra of Fe NP in the RMS with values ω1=1.5, ω2=3.0, ω3=5.0 (1 day after the synthesis) are shown in Fig. 1.

The results of changes in the optical absorption spectra due to the evolution of the NPs (Chem) obtained in the RMS, depending on the storage time of samples are shown in Fig. 2 and Table 2.

On the base these results (Fig. 1 and 2) we can conclude that in the optical absorption spectra of Fe NPs RMS have after 1 day a weakly expressed band with λ_{max}~215 nm, 270 nm, 343 nm, and only for RMS solution of Fe NPs (ω=1.5) was recorded an additional band at λmax~425 nm. As you can see the intensity of the optical absorption depends on the value of ω in the Fe NPs RMS , i.e., on the content of iron ions in the solution. Depending on the time the increasing of the optical density was observed in all samples, after a time interval Δt > 20 days the "saturation" was succeeded. The resulting Fe NPs are stable in the RMS and in the adsorbed state on the surface of different composites.

Radiation-chemical reduction method (RadChem). The aqueous solution of 0.3M Mohr's salt $((NH_4)2Fe(SO_4)2*6H_2O)$ was injected into 0.15M AOT/isooctane solution in accordance with the selected coefficient values of solubilization equal molar ratio ω=[H_2O]/[AOT]. To remove oxygen,

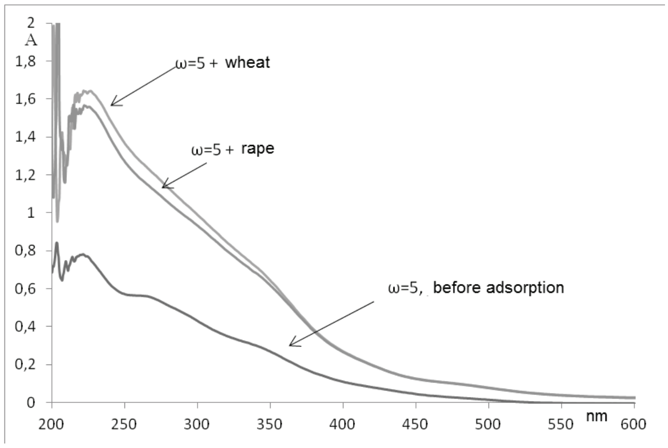

Fig. 5. Fe NP (Chem) RMS ω=5,0 optical absorption spectra changes after the contact with AC samples obtained from wheat and rape within 3 days. Reference –0.15M AOT/isooctane

Rys. 5. Fe NP (Chem) RMS ω = 5,0 zmiany widma absorpcji po kontakcie z AC próbek uzyskanych z pszenicy i rzepaku w ciągu 3 dni. Odniesienie -0.15M AOT/izooktan

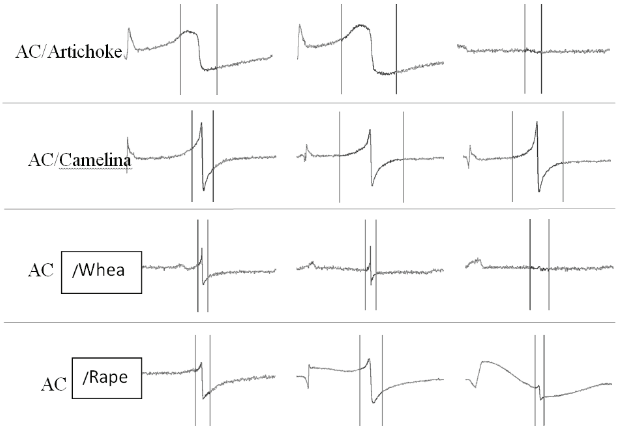

Fig. 6. EPR spectra of the plant AC samples from Jerusalem artichoke, camelina , wheat , and rape – prior and after irradiation at a dose of 20 kGy, and after contact with Fe NP (Chem) RMS

Rys. 6. Widma EPR próbek roślinnych AC z topinamburu, lnu, pszenicy i rzepaku – przed i po napromieniowaniu w dawce 20 kGy, a po kontakcie z Fe NP (che) RMS

micellar solutions were saturated by argon, sealed and irradiated with γ-rays at the facility 60Co RHM-γ-20. The radiation dose was 19.7 kGy. In the method of radiation-chemical synthesis the reduction of metal ions is due to the interaction with short-lived products of water radiolysis having reduction properties: solvated electrons e-solv, H-atom and the radicals R(i). The oxidative component of water radiolysis the OH-radical by reaction with isopropyl alcohol molecule enters recovery oxiisopropyl radical which involved in the ion reduction reaction and increases the Fe NP yield.

The spectra of Fe NPs (RadChem) in RMS (Fig. 3) exhibit intense, though not well-resolved, optical absorption bands at 200-500 nm, which position is similar to spectra of Fe NPs (Chem) in RMS, which are weaker in intensity. The results obtained by measuring the optical absorption (OA) as a function of storage time (Δt) of the samples, have confirmed stability of NP Fe (RadChem).

Adsorption properties of Fe NP (Chem)

Using the method of UV-VIS spectrophotometry, changes in the Fe NP (Chem) RMS OA spectra were recorded depending on the time of various plant AC samples retention in the solution. Fig. 4 and 5 show comparison of spectra of initial NP RMS, and those after 3 days of contact with various ACs (the volume ratio of Fe NP RMS and AC ~ 1: 1).

The Increase of Fe NP RMS ω=3,0 spectra intensity after the contact with AC surface is evident on Fig. 4. The highest growth was observed for the solution after the contact with Jerusalem artichoke sample. Spectra properties prove “NP post-formation” in the solution at early stage, as a result of the reaction of the remaining metal ions – still present in the RMC along with NP – with active centers on the surface of the adsorbents. After 5 ÷ 6 days OA of Fe NP RMS ω=3,0 reached the highest Fe "NP-saturation" level, followed by usual decline of OA values characteristic of NP concentration decrease due to NP adsorption on the AC surface and inside the pores. Similar increase of the metal NPs content in the solution due to "post-formation" (after-formation) was noted [14] within the study of the adsorption of palladium nanoparticles (Pd NPs) on the silica gel. Optical density increase at "NP-saturation" stage of the solution (by almost 50%), and its decline at the second stage, when NP adsorption became the predominant process, was determined during the contact of Fe NP in RMS ω=5,0 with wheat and rape ACs, as shown on Fig.5.

Attention should be paid to NP concentration increase in Fe NP (RadChem) RMS during its contact with the AC surfaces, though recorded the optical density changes did not exceed 5 ÷ 6%, showing much lower increase data, than in the experiments run with Fe NP (Chem) RMS. It can be suggested, that more active extra NP "post-formation" in presence of certain adsorbents, when chemical reduction of metal ions is used for NP synthesis, is related to quercetin, which has known chelatic properties. For example, quercetin application to the surface of the coal filter's surface used to increase its adsorption capacity and selectivity for heavy and radioactive elements [15]. However, conclusion on the mechanism of the formation process of additional Fe NP and possible explanation of the differences of this reaction due to different methods of synthesis, used adsorbent's properties require additional studies and modern experimental techniques, including EPR [16,17].

The paramagnetic properties of plant active carbons. Using EPR method the authors [16-19] have proved existence of paramagnetism in the carbons, which was associated with the presence of at least two different types of reaction centers: constituted by trapped electrons, or by free radicals in the conjugated aromatic systems. The signals of these centers overlap but have different values of the g-factor. Structural changes in coal get revealed in changing correlation of the narrow and wide signal and g-factors shifts, which can be detected on the EPR spectra.

With the use of EPR we have assessed the paramagnetic properties of plant active carbons after grinding and after radiation treatment of the dry samples.

EPR data in Fig. 6 show spectra of the plant AC samples samples from residues of different cultures: Jerusalem artichoke, camelina (II), wheat (III), rape (IV), all samples of same weight, - prior and after irradiation at a dose of 20 kGy, and after contact with Fe NP (Chem) RMS.

Obtained results suggest: 1) that the type of the AC sample affects the structure and intensity of the ESR spectra (Fig. 6,I-st and the II-th columns), 2) that exposure of four studied AC samples to ionizing radiation (20 kGy) does not lead to the destruction of the paramagnetic centers, which proves their high radiation stability. Research has proved significant impact of adsorbed Fe NP on EPR signal parameters (Fig. 6, III-rd column) of the paramagnetic centers. It can be concluded, that interaction of Fe NPs with AC paramagnetic reaction centers is partially responsible for adsorption of metal nanoparticles.

Thus, by performing additional modification of active carbons on the basis of plant waste from rapeseed, camelina, Jerusalem artichoke and wheat, - with Fe nanoparticles, new carbon nanomaterials with specific properties and biological activity were obtained. During the field testing described composites were applied to seed surface as (nano) chips, and proved prospective of their future use for pre-processing of oilseed brassica crops. It was shown that pre-sowing seed treatment significantly stimulates the development of seedlings, and increases plants resistance to the stress in unfavorable growth conditions [20].

Literatura – References

1. Fedorenko, V.F. Overview of the Russian nanopreparation for processing of agricultural crops. Buklagin, D.C.; Golubev, I.G.; Nemenutshaya, L.A. Rossiiskie Nanotekhnologii. 2015. v.10 -№3-4. P.126-131.
2. Nabeeva, R.A. Influence of growth regulators on Pro - and antioxidant system of wheat sprouts. Farhutdinov, R.G.; Fedyaev, V.V.; Hairullina, R.R.; Ibragimov, A.G. Collection of materials of All-Union. Sci. Conf. with Int. participation "Fundamental and applied problems of modern experimental biology of plants. Moscow. 2015. P.464-468.
3. Kovalenko, L.V. Ultrafine powders in the solution of the food independence of Russia. Pavlov, G.V.; Folmanis G.E. and others. Proceedings of the Conference "Physicochemistry of ultrafine systems. Obninsk. 1998. P. 211.
4. Gusev, A. A. Morphometric Parameters and Biochemical Status of Oilseed Rape Exposed to Fine-Dispersed Metallurgical Sludge, PHMB-Stabilized Silver Nanoparticles and Multi-Wall Carbon Nanotubes. Akimova, O. A.; Zakharova, O. V.; Godymchuk, A. Y.; Krutyakov, Y. A.; Klimov, A. I.; Denisov N. A.; Kuznetsov, D.V. Advanced Materials Research. – 2014. – P.212-218.
5. Biologically active multifunctional nanochips and method of application for production of high-quality seed. Ruban, I. N.; Voropaeva, N. L.; Figovsky, O. L.; Sharipov, M. D.; Dadajanov, T. K. U.S. Patent № 8209902. – 2012.
6. Revina, A.A. Modified (nano)particles of silver and iron adsorbents based on activated carbons. Voropaeva, N.L.; Mukhin, V.M. and others. Abstracts. I Int. scientific-practical Conf. "Graphene and related structures: synthesis, production and application". – Tambov. – 2015. – P.165-167.
7. Chekmar, D.V. Effect of modification of carbon materials on the adsorption of NP silver. Tanasyuk, D.A.; Voropaeva, N.L.; Revina, AA. Materials of II All-Union. Conf. with Int. particip. and Symposium "Topical problems of theory of adsorption, porosity and adsorption selectivity". Moscow, Klyazma. 2015. P. 76.
8. Voropaeva, N.L. Recultivation of plant wastes (straw) and obtaining (nano) chips with bactericidal properties based on them. Mukhin, V.M.; Revina, A.A.; Busev, C.A.; Karpachev, V.V. GeoScience Engineering. – 2015. – Vol. LXI. – N 3. – P. 1-7.
9. Method of obtaining active coal from plant waste. Mukhin, V.M.; Voropaeva, N.L.; Karpachev, V.V.; Spiridonov, Yu.Ya. and others. RF patent № 2527221. – 2014.
10. A method of producing activated carbon from plant material – straw cruciferous oilseeds. Mukhin, V.M.; Karpachev, V.V.; Voropaeva N.L. and others. Patent RF № 2562984 РФ. – 2015.
11. Voropaeva, N.L. Modified natural raw materials and products recycling of waste consisting of environmentally safe (nano)chips for APK. Karpachev, V.V. and others. Ecological Bulletin of the North Caucasus. – 2015. V. 11. № 1. – P. 31-34.
12. The preparation of nanosized particles of metals and method for its production. Revina, A.A. Patent RF № 2312741. – 2007. – Bull. № 35. – 20.12.2007.
13. The preparation of nanostructured particles of metals and method for its production. Revina, A.A. Patent RF № 2322327. – 2008. – Bull. № 11. – 20.04.2008.
14. Revina, A.A. The study of the adsorption of palladium nanoparticles on silica by methods of spectrophotometry and atomic force microscopy. Belyakova, L.D.; Parkaeva, S.A.; Souvorova, O.V.; Sergeev, M.O.; Zolotarevski,V.I. Physical chemistry of surfaces and protection of materials. 2010.V.46.№6. 448-454.
15. The method for producing a modified activated carbon. Revina, A.A.; Mukhin, V.M. and others. Patent № 2104927. – 1998. – Bull. – 20.02.1998.

16. Losev, B.I. et al. Paramagnetic resonance in fossil coals. Reports of USSR Academy of Sciences. – 1959. – V. 125. - № 4. – P.814-816.

17. Adashkevich, S.V. About correlation of technological and radiospectroscopic parameters of coals. Lapchuk, N.M.; Lapchuk, T.M.; Oleschkevich, A.N.; Steljmakh,V.F.; Fan Suan Toan; Schilardi, G.O. Proceedings of the 5th Int. Scientific Conf. "Materials and structures of modern electronics". Belarus/Minsk. 2012. P.10-12.

18. Rusyanova, N.D. Coal chemistry. – M.: Nauka. – 2003. – 316 p.

19. Retcofaky, H.L. EPR g- values of coals. Stark, I.M.; Fiedel, R.A. Chemistry and Industry. 1967. Vol. 31. - № 5. P. 1327-1328.

20. Voropaeva, N.L. Reclamation of plant wastes (straw) and obtaining (nano) chips with bactericidal properties based on them. Mukhin, V.M.; Revina, A. A.; Busev, S.A.; Karpachev, V.V. GeoScience Engineering. – 2015. – Vol. LXI. – 2015. - № 3. – P. 1-7.

Wpływ nanoczateczek żelaza na właściwości fizyko-chemiczne i wykorzystanie węgla aktywnego z materiałów roślinnych

Materiały odnawialne w postaci odpadów roślinnych (słoma) roślin typu: rzepak, len, pszenica, topinambur przetworzono na węgiel aktywny którym poddano modyfikacji za pomocą nanocząsteczek żelaza, tak aby uzyskać materiał o właściwościach sorbcyjnych. Sorbenty są powszechnie stosowane w przemyśle spożywczym, rolnictwie, medycynie i innych dziedzinach działalności ludzkiej.

Słowa kluczowe: węgiel aktywny, nanocząteczki Fe, materiały użyteczne, własciwości paramagnetyczne, odpady organiczne, technologia modyfikacji