THE USE OF METAL NANOPOWDERS FOR THE PRESOWING TREATMENT OF SEEDS

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Abstract

The test results of mixtures for the presowing treatment of seeds of sugar-beet, table beet, barley and spring wheat with the use of nanopowders of copper, iron and zinc (Cu, Fe, Zn nanopowders) are described in the article. During the experiments with sugar-beet seeds and table beet seeds the protective properties of nanopowders appeared not only towards fungoid diseases but also towards weevils. The treatment of seeds with nanopowders and Adifur ensured the protection of young crops against black root of sugar beet during the intentional infection at the Thtram insecticide level. The efficiency of seeds treatment with nanopowders against leaf eating insects was marked only at the first stages of plant development. During the experiments on the presowing treatment of barley seeds with nanopowders the positive influence on crop yield was marked. The spring wheat (Lada, Amir, MIS varieties) specific features for the presowing treatment of seeds with nanopowders were defined. Lada variety was injured with brown rust and septoria leaf spot in less degree and MS variety' showed the highest productivity' increase while treating with nanopowders. The protein content increased greatly in Amir variety seeds and the content of moist and dry gluten in the Lada variety flour also increased.

Metals-nanoparticles in size 10-50 nanometers in the ultra dispersed form are known to acquire the unique properties used in various industries. The bactericidal properties and the possibility to use metal nanopowders as microelements are most interesting for biologists.

The microbicidal effect of copper nanopowders is shown. The growth inhibition with copper nanoparticles of gram-negative bacteria E. Coli K-12 (glucose-mineral environment) constituted 80% E,, Coli AB 1 157 - 35% and gram-positive bacteria St Albus - 60% [1].

The toxicity line of metal nanopowders on parameter $LD_{50:}$ Cu>Zn>Fe>Cr>Al=Ag has been revealed and the lower toxicity level in comparison with salts of analogical metals has been defined. So, on parameter LD50 copper sulfate is in 7,5 times more toxic than copper nanopowder, zinc sulfate in 28 times more toxic than zinc nanopowder, ferric sulfate is in 36 times more toxic than ferric nanopowder [1]. This allows to use nanopowders efficiently in the composition of premixes and mixed fodders as the source of microelements [2, 8].

The idea to use metal nanopowders for the crop seeds disinfection belongs to S.V. Krylov who headed the laboratory for crop seeds hydrophobization at Timiryazev Agrarian Academy in 1972-1994. S.V. Krylov developed the following method of seeds hydrophobization: seeds were treated with polysterene dissolved in chloroform. This polysterene formed the protective film which contained pesticide Fenthiuram [5]. This method allows to sow crops (first of all, corn) in early spring and to protect crops against diseases and pests. However, S.V. Krylov tried to improve the method of seeds hydrophobization and make it safe. He chose the method of using metal nanopowders instead of pesticides. The logic of S.V. Krylov was as following: nanoparticles of metals are electrically neutral and they are distributed uniformly in the film-forming material covering seeds and ensuring their reliable protection against pathogens. Oxidizing in the soil progressively, nanopowders produce unfavorable conditions for pathogenic microorganisms and are used by plants as microelements in the growth process.

In cooperation with producers of metal nanopowders S.V. Krylov conducted the laboratory and field experiments and included copper, iron, zinc and molybdenum nanopowders in the composition of seed hydrophobic cover instead of pesticide Fenhtiuram, i.e. he tried to protect seeds and crops without using pesticides and at the same time provide plants with microelements. On the basis of conducted research and production tests the mixture containing hydrophobic polymer and metal nanopowders was produced. The metal nanopowders in this mixture protect seeds and crops against pathogens at the pesticides level and stimulate the growth and development of plants by reducing the vegetative period. The mixture was protected by the patent of the Russian Federation № 2074616 dated 10.03.1997 [6].

In the test laboratory the combined mixtures including the nanoparticles of various metals (Cu, Fe, Zn, Mo) were tested and the optimal proportions of components were experimentally defined. The disinfectant and stimulating effect of Cu, Fe, Zn, Mo nanopowders while seeds treating was shown by direct and indirect methods [7, 9 - 13, 15]. However, due to the perestroika period in the former USSR the ecologically safe technology of seeds disinfection without using pesticides was not applied in agriculture. Besides, the seeds hydrophobization method developed by S.V.Krylov had a significant defect due to organic dissolvent (chloroform) using for forming a film over treated seeds. So the further development of the seeds presowing treatment technology with the use of metal nanoparticles was aimed at the improvement of mixtures and film-forming materials [4, 9, 11, 13,14].

As a research result in the field of metal nanopowders using for the seeds presowing treatment the water-soluble polymers were discovered. These polymers also did not require the toxic organic dissolvents. This made the seeds treatment process easier and reduced the mixture cost.

The work on using metal nanopowders in combination with insecticides and pesticides in order to reduce the doses of pesticides while seeds treating was also conducted. The research work on the development of the new generation of bactericidal and fungicidal mixtures made on the basis of metal nanopowders and polymers for seeds and vegetating plants treatment is being conducted [13].

Some research results on the efficiency of metal nanopowders using in the technology of seeds presowing treatment for the plant protection against diseases and pests and on the metal nanopowders influence on the yield quality are given below.

The research objects and methods

The research was conducted in cooperation with the staff of All-Russian scientific and research institute of sugar beet and sugar (ВНИИСС) named after A.L. Mazlumov (the city of Ramon, Voronezh region); All-Russian scientific and research institute for plant protection (ВНИИЗР) (the Institute test field, Voronezh region, Ramon area) and the Department of spring crops selection at State scientific and research agricultural institute for central regions of non-chemozemic zone (ГНУ НИИСХ ЦРНЗ) .

The sugar beet seeds in the production conditions are treated with the pesticides and insecticides complex before sowing or the pelleted seeds are used. At this about 6 kg of pesticides is applied for 1 ton of seeds to control black root of beet and the same amount of insecticides is used to fight against beet flea-beetle and other pests. In order to increase the beet yield and protect environment the research on reducing dose of applied pesticides by replacing them with metal nanopowders and other mixtures was conducted.

Authors are very grateful to E.I. Khrukina, Ph. D. in Agriculture, Head of Pesticides Testing Laboratory at ВНИИЗР, A.V. Lazukin, associate researcher and N.V. Davydova, Ph. D. in Agriculture, Head of Spring Wheat Selection Laboratory for their support in research.

The seeds before sowing were treated with the composition including the mixture of metal nanopowders (copper - 60%, zinc - 20% and iron - 20%) with hydrophilic film-forming material - 5% NaCMC. The rate of treatment with Cu, Fe, Zn nanopowders was calculated in diapason from 0,25 to 2,0 kg of nanopowders per one ton of seeds.

At ВНИИСС and ВНИИЗР the seeds of sugar beets (variety Voronezhskaya 1990), table beet (variety-Dvusemyanaya TSKHA) and barley (variety Odessky 100) treated with nanopowders were sown. The test sowings were applied at plots of land - 10 m^2, location - at random, repetition rate - 4-divisible. During the laboratory tests a week after the presowing treatment the barley seeds were infected with head smut chlamydospores.

In ГНУ НИИСХ ЦРНЗ experiments on the presowing treatment of spring wheat seeds the plot of land area was 12 m^2, repetition rate 4-divisible, the rate of sowing - 6 mln. germinating seeds per 1 hectare taking into account the germinating power of seeds.

The sugar beet (variety Voronezhskaya 1990) seeds were treated with the mixture of Cu, Fe, Zn nanopowders at rate 0,25, 0,5 and 1,0 kg/ton of seeds and 35% Adifur in the film-forming material NaCMC solution.

The influence of nanopowders treatment on the germinating energy of seeds while intentional infecting them with black root of beet was studied in the laboratory. The influence of seeds treatment on the crops injury by black root of sugar beet and the resistance of plants to insects and leaf eating pests were defined on the ВНИИСС test field. The seeds treated with Thiram were used as a standard.

Results and their discussing

The seeds of sugar beet (variety- Voronezhskaya 1990) were treated with the mixture of metal nanopowders Cu, Fe, Zn at the consumption rate 0,5; 1,0 and 2,0 kg/ton of seeds and 50% Adifur in the film-forming material NaCMC solution. The treatment influence on the energy of seeds germinating while intentional infecting them with black root of sugar beet was studied in the laboratory. The crops injury by black root of sugar beet and the resistance of plants to leaf eating pests were defined during field tests.

The assessment results of the biological efficiency of sugar beet (variety Voronezhskaya 1990) seeds treatment with the mixture of nanopowders Cu, Fe, Zn and 50% Adifur against black root of beet are shown in Table 1.

The treatment of seeds with nanopowders Cu, Fe, Zn in the concentration 1 and 2 kg per ton of seeds (combined with Adifur) ensured the protection of seeds against black root of sugar beet while intentional infecting them at Thiram insecticide level. This insecticide is used in the production for the treatment of sugar beet seeds [3]. The field germinating power in all variants of treatment with nanopowders Cu, Fe, Zn differed insignificantly from the variants when seeds were treated with insecticides. The number of diseased plants was less than in the control variant and didn't exceed the variant when seeds were treated with Thiram at the nanopowder consumption rate-2 kg/ton. The best results were obtained during the treatment with Tachigaren (70% powder possessing wetting ability) but this variant is the worst one from the ecological point of view.

While treating seeds with nanopowders Cu, Fe, Zn in concentration 2kg/ton of seeds the positive effect in the protection against leaf-eating insects during the first development phases (crops and fork) was obtained. In the phase 1-2 pairs of true leaves the protective role of nanopowders Cu, Fe, Zn was not revealed for certain. The treatment with 35% Adifur at the rate 30 l/ton was more effective (Table 2).

Tabl 1

Biological efficiency of sugar beet (variety-Voronezhskaya 1990) seeds treatment with nanopowders Cu, Fe, Zn against black root of sugar beet
(ВНИИСС, the city of Ramon)

Variant	Rate of mixture consumption kg/ton	Germination energy (laboratory, artificial background), %	Field germination, %	Degree of crop infectiousness with black root of sugar beet, %	
				number of diseased plants	disease development
Control	-	100,0	88	44,3	28,4
Tachigaren 70% powder possessing wetting ability	6,0	89,7	88	18,1	8,8
Thiram 80% powder possesing wetting ability	6,0	94,8	91	33,7	21,3
Nanopowder Cu, Fe, Zn + Adifur 50%	0,5	71,0	87	47,1	32,0
Nanopowder Cu, Fe, Zn + Adifur 50%	1,0	89,7	81	37,0	25,7
Nanopowder Cu, Fe, Zn + Adifur 50%	2,0	100,0	84	35,4	23,0
LSD $_{0,5}$			6,6	6,2	

Table 2

Biological efficiency of sugar beet (variety-Voronezhskaya 1990) seeds treatment with nanopowders Cu, Fe, Zn against leaf-eating insects
(ВНИИСС, the city of Ramon)

Variant	Rate of mixture consumption	Injury of plants in phase, %		
		sprouts	fork	1-2 pairs of true leaves
Control	-	9,1	18,1	13,9
Adifur, 35% liquid paste	30 l/ton	1,8	3,9	6,5
Nanopowders Cu, Fe, Zn	2 kg/ton	4,9	8,9	12,9
LSD 0,5	-	1,3	2,3	2,8

So, the partial replacement of pesticides with ultra dispersed metal powders in the conducted experiments showed the possibility to use them in order to reduce the soil loading and the environment burden due to the use of pesticides. The treatment of seeds in concentration 2kg/ton of seeds ensured the protection of crops against pathogens at Thiram level. The most important research result is that the seeds treatment with nanopowders Cu, Fe, Zn in the maximal concentration (2kg/ton) influences greatly the crops protection against leaf-eating insects. It seems reasonable to conduct further research in order to specify the concentrations of nanopowders Cu, Fe, Zn and include other metals into the mixture as well as to research the possibility to replace pesticides with nanopowders Cu, Fe, Zn in order to reduce the dose of insecticides used while sugar beet seeds treating.

While treating table beet seeds with nanopowders Cu, Fe, Zn in combination with insecticide Carbosulfan plants didn't suffer from pests and diseases. The yield of roots while table beet seeds treating with nanopowders was 15-18% higher than in the control group. In the control variant the significant injury of plants with cercospora leaf spot and weevil while seeds treating with Thiram and crops spraying with insecticides was marked (Table 3).

Table 3

Field germination of seeds, degree of plant infectiousness and yield of table beet (variety-Dvusemennaya TSKHA) while seeds treating with nanopowders Cu, Fe, Zn in combination with insecticide (ВНИИСС, the city of Ramon)

Variant	Rate of mixture consump-tion	Field germina-tion, %	Degree of plant infectiousness, %		Yield, centner/ha	Deviation from control	
			Cercospora leaf spot	Weevil		centner/ha	%
Standard Thiram + Carbosulfan (crops treatment)	10 kg/ton 3 kg/ha	98	30	70	300	-	-
nanopowder Cu, Fe, Zn + Carbosulfan (seeds treatment)	0,3 kg/ton 3 kg/ton	100	-	-	360	60	18
nanopowder Cu, Fe, Zn + Carbosulfan (crops treatment)	0,3 kg/ton 3 kg/ha	100	-	-	345	45	15

In the experiments on the presowing treatment of barley seeds with nanopowders Cu, Fe, Zn their positive influence on the crop productivity is shown in (Table 4).

Table 4

Economic efficiency of the presowing treatment of barley (variety-Odessky 100) seeds with nanopowders Cu, Fe, Zn (ВНИИЗР test field)

Experiment variants	Rate of mixture consump-tion, kg/ton	Yield structure				Yield centner/ha	Yield increase centner/ha
		Ear length, cm	Number of seeds in a ear, items	Weight of seeds in a ear, gram	Amount 1000 seeds, gram		
Control	-	5,33	14,37	0,63	44,11	23,9	-
Nanopowder Cu, Fe, Zn + hydrophobic poly-mer	0,3	5,72	16,22	0,74	45,66	26,6	2,7
Nanopowder Cu, Fe, Zn + hydrophobic poly-mer	0,5	5,50	15,43	0,69	44,91	24,9	1,0
Nanopowder Cu, Fe, Zn + NaCMC	0,5	5,29	15,77	0,69	43,53	24,7	0,8
Nanopowder Cu, Fe, Zn + NaCMC	0,3	5,66	16,55	0,75	45,31	25,5	1,6
LSD_{05} =						2,14	

The significant yield increase could be observed during the treatment of barley seeds with nanopowders Cu, Fe, Zn while using the hydrophobic polymer as a film-forming material [6] at the nanopowder consumption rate 0,3 kg/ton of seeds. The use of water-soluble NaCMC at the same consumption rate of nanopowders did not produce the significant positive effect.

The information on the specific reactions of spring wheat varieties to the presowing treatment of seeds with nanopowders Cu, Fe, Zn appeared to be interesting. The spring wheat (Lada variety) grown from the seeds treated with Cu, Fe, Zn, nanopowders was injured with brown rust and septoria leaf spot in the definitely less degree but variety MIS showed the greater yield increase while treating with nanopowders. The spring wheat (variety Amir) seeds treatment with nanopowders influenced significantly the content of protein in a seed (table 5).

Table 5

Results of metal nanopowders testing on spring soft wheat
Department of spring crops selection
ГНУ НИИСХ ЦРНЗ

Variety, test variant	Crop yield, centner/ha	Injury with diseases, %		Plants number per meter, items.	Ear length, cm	Weight of seed in a ear, gram	Protein %
		Brown rust	Septoria				
Lada, without treatment with nanopowder	59,9	15	20	61.8	7,9	0,95	13,55
Lada, treatment with nanopowder	62,6	5	15	63,2	8.8	1,29	13,61
Amir, without treatment with nanopowder	64,1	35	25	58,2	8,4	1,26	13,08
Amir, treatment with nanopowder	61,5	15	20	70,0	8,3	1.21	13,59
MIS, without treatment with nanopowder	55,5	5	40	89,5	7.3	0,95	12,86
MIS, treatment with nanopowder	59,4	5	30	111,5	7.5	1.0	13.05

The significant influence of the presowing treatment of seeds with nanopowders Cu, Fe, Zn on the quality of spring wheat seeds (varieties Lada, Amir and MIS) was defined (Table 6). The content of moist and dry gluten in wheat flour increased significantly. It was especially clearly seen in the case of Lada variety. Probably this fact may be explained by the wheat reaction to the treatment of seeds with nanopowders Cu, Fe, Zn as to the additional supply of necessary microelements.

Table 6

Results of technological analysis of samples of spring wheat (varieties Lada, Amir and MIS) grown from seeds treated and untreated with nanopowders Cu, Fe, Zn (ГНУ НИИСХ ЦРНЗ)

Variety, test variant	Weight 1000 seeds	Gluten in flour		
		% moist	Gluten deformation Indicator, scale units	% dry
Lada, without treatment with nanopowder	41,8	21,3	52	8,7
Lada, treatment with nanopowder	42,8	36,0	60	12,8
Amir, without treatment with nanopowder	36,8	31,3	58	10,8
Amir, treatment with nanopowder	38,0	33,5	72	11,4
MIS, without treatment with nanopowder	40,0	23,6	46	8,4
MIS, treatment with nanopowder	40,8	31,6	47	11,2

It is known that copper, iron, zinc and molybdenum are vitally important mineral elements necessary for plants as microelements. They are also used as micro fertilizers in the form of mineral salts in agriculture. The main method of using is applying before sowing in combination with seeds in amount 0,5 - 5,0 kg/ha of active substance.

The use of metals Cu, Fe, Zn as microelements in the form of nanoparticles, i.e. in the non-ionic form for seeds treatment (for example, wheat) at consumption rate 0,5 - 2,0 kg/ha is ecologically safe as in such case the number of applied metals decreases in several times in comparison with the recommended doses in the form of mineral salts. The metal nanopowders while seeds treating fall into soil locally but in such small amounts they cannot contaminate soil. It also should be marked that it possible to mix metal nanopowders and reduce proportionally the amount of metals.

The use of metal nanopowders is the ecologically pure technology. It excludes pesticides using or reduces significantly their doses while agricultural crops cultivating. Besides, the additional equipment is not required as this technology may be applied in

combination with other kinds of treatment including biologically active compositions. The suspension with nanopowders is not toxic (4th class of danger) and does not possess any smell. So it is safe and does not require the protection of staff while seeds and plants treating.

The technology may be used for the treatment of seeds of various crops before sowing, for vegetating plants spraying, for the roots treatment as well as for the protection from such diseases as loose smut, Helminthosporium spot disease, downy false mildew, Ascochyta blight, rots, etc. The mixture with nanopowders stimulates the germination of seeds by increasing their energy and germinating power and it allows to obtain ecologically pure products.

SUMMARY

The fungicidal and insecticidal effect of nanopowders of copper, iron and zinc while including them into mixtures for the presowing treatment of seeds is shown on some agricultural crops. The treatment positive effect on the crop productivity and the quality of spring wheat seeds has been defined.

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