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The Efficancy of Micron and Nanoscale Sulfur the Schutte Fungi

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Abstract: Investigations of antifungal activity of micron and nanoscale forms of sulfur on two types of pathogenic Schutte fungi have been studied. As micronized sulfur used crushed in a roller mill, and as nanosized sulfur precipitated from a solution of sodium polysulfide. The size and shape of the particles of sulfur were characterized using a laser analyzer and probe microscope, the structure by X-ray diffractometer. Antifungal effects of sulfur particles in Sabouraud medium and field expierence have been studied. It is found that in all cases of laboratory and field expierence, antifungal activity of nanosized sulfur with an average particle size of 25 nm, 5-10 times higher than the sulfur micron with an average particle size of 8 microns. The results can be used to create more effective than conventional sulfur plant protection products.

Keywords: sulfur, nanoparticles, dispersion, fungicide, Schutte fungi.

1. Introduction

Recently, with the development of technical research capabilities, particularly relating to the analysis and observation of matter particles with sizes less than 100 nm have opened vast prospects for observation of phenomena occurring at the nanoscale. The result was the development of methods for the preparation of nanoparticles of different chemical nature, are active (chemical, catalytic, biological) activity of particles much larger than the macroscopic and micron scale. Huge observational data collected in the world over the last 10 years in the field of nanotechnology, in particular in the field of obtaining ultrafine nanoscale materials with unique properties radically changed the situation in the field of modern chemical engineering and materials science.

In particular, high specific surface area of nanomaterials leads to the fact that surface phenomena (adsorption, desorption, adhesion) are beginning to play a predominant role in their interaction with macroscopic materials, with macromolecules and biological objects. The consequence of this is to increase the efficiency of the biological effects of conventional formulations, with even low concentrations of nanoparticles has no significant toxic effects, can produce a significant impact on living organisms.

As well as many other substances, sulfur is a very attractive target for application of nanotechnology, as its main areas of application are connected with the use of its properties in the dispersed state. Due to the high efficiency, no long-term consequences for health and enough cheap drugs (medicine and agriculture) on the basis of elemental sulfur in great demand today. Disperse sulfur micron size, obtained by grinding in mills of various designs are widely used in various fields of industrial production. agriculture, rubber industry for curing and synthesis of various chemical products. [1]. The efficiency of the use of sulfur in these areas significantly increases with decreasing particle size. Since you cannot get sulfur submicron range by a direct grinding, so now a proliferation of a variety of effective methods for the preparation of nanoparticles of sulfur have been developed, mainly by methods of chemical deposition from different nature solutions [2-8]. At the same time, research on the biological effects of nanoparticles sulfur few published [2, 6-8].

Now it is well known that the difference in size, especially in the transition to the nano range, strongly affect the biological activity. In [2] it was experimentally established that the use of nanoparticles with an average particle size of 10-15 nm in bacteria, yeast and fungi strains is more effective than the 80-100 nm. Current research aimed at comparing the biological effects of sulfur particles of micron and nano range relevant [6,7] as well as for many other promising biologically active substances. In [6,7] on assessing the impact of sulfur nanoparticles on the growth of shoots and roots of wheat in the early stages of development has been experimentally established the high efficiency of nanoscale sulfur with an average size of 20-25 nm. Detailed studies of the antifungal activity of micron and nanoscale sulfur using ten kinds of different

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strains of fungi have been conducted in [8] and as a result it was found that the antifungal activity of nanoscale sulfur to 4-9 times higher than that of micronized sulfur. [6-9] show that the creation of products based on nanoscale sulfur will significantly improve the efficacy of this line of action. At the same time, the use of nanoparticles of sulfur requires the development of new methods for determination of sulfur in nanoforms [10].

But along with the pathogenic fungi, parasites in humans and animals there are plenty of plant parasitic fungi to combat that use various fungicidal agents.

Well known examples of successful use of sulfur to protect plants from fungal diseases and herbivorous mites. For plenty of years, sulfur in the form micron-sized sulfur powder [11-12] has been extensively and effectively used as a fungicide and acaricide in agriculture. In the Soviet Union and Russia micron-sized sulfur powder was used according to specifications [13-14].

In this paper, two types of fungi affecting forest consisting of pine trees, which are very valuable trees. The economic significance of forest tree diseases is extremely high. Under current conditions, despite the known achievements in breeding resistant varieties, creation and use of various means of combating plant diseases, many diseases still bring harm Forestry. In nurseries often mass mortality of seedlings of trees from the lodging and disease type Schutte (Schütte), caused by pathogenic fungi. Common representatives of pathogenic fungi are common type Schutte (pathogens - fungi marsupials Lophodermium), and snowy Schutte (pathogen - Tasmanian mushroom Phacidium infestans) [15]. The disease is especially dangerous for Schutte nurseries. Signs of the disease with lesions common Schutte is yellowing, then browning and shedding of needles (see Fig.1b), snow Schutte disease manifests as a white bloom on the needles, like the snow (see fig.1c).

For successful use of antimicrobials in agriculture as a means of plant protection requires that they combine environmental friendliness, reasonable price and high efficiency. It is well-known environmental safety of sulfur. The long history of sulfur use in agriculture indicates no adverse long-term consequences of the use of sulfur-based drugs. Availability on the market a huge number of high-quality and low-cost sulfur produced during the purification of oil and gas from the sulfur can be used as a raw material for its products on the basis of the available amount. An increase in the effectiveness of drugs based on sulfur as shown in [6-8,16,17] can be achieved by the use of nanoparticles of sulfur. In this regard, this paper presents a comparison of the fungicidal properties of the various different forms of sulfur, micronized sulfur, obtained by grinding in a roller mill and nanoparticles prepared by chemical precipitation from aqueous polysulfide solution as in [6-8,16,17].

Antifungal activity of sulfur was studied in laboratory and field experiments. Schutte developments of fungi were studied in the laboratory in Sabouraud medium. Myceliums were placed in Petri dishes containing culture medium, then the diameter of the colonies was measured at different concentrations of sulfur. Along with laboratory tests were also carried out and field tests on pine seedlings in the nursery. In this case, we measured the number of infected plants after a single treatment in each of the plots using different concentrations of sulfur. In both types of experiments were conducted to compare the data with those for untreated samples.

2. Materials and Methods

To conduct the study, we used the following reagents are "chemically pure" skills: elemental sulfur S crushed in a roller mill, calcium hydroxide, $Ca(OH)_2$. All the chemicals were used without further purification. For the preparation of medium white powder agar - agar, which is a natural product used Ahnfeltia algae taken from the White Sea. In this paper, were used fungal strains that are grown in a research institute of technology herbicides and plant growth regulators of the Academy of Sciences of the Republic of Bashkortostan.

To obtain micronized sulfur we used elemental sulfur, crushed in an industrial roller mill, and for the preparation of nanoparticles of sulfur used by chemical vapor deposition from an aqueous solution of calcium polysulfide. Particle size distribution of micronized and nanosized sulfur was determined by particle size analyzer Shimadzu SALD - 7101. To determine the size and shape of the particles of sulfur was used scanning probe microscope Solver Pro M. Analysis of the structural characteristics of the samples was performed on X-ray diffractometer Rigaku Ultima IV.

3. Results

3.1. Obtain samples of sulfur in micro-and nano-range

Integral and differential distribution of sulfur particles by size, obtained after grinding in a roller mill is shown in Figure 2, in the form of black circles (●). From the presented data in (Figure 2) shows that the distribution of the particles in this case is in the range from 2 microns to 50 microns, and the average size is 8 microns.

Calcium polysulfide was produced by a chemical reaction between the ground in a roller mill of elemental sulfur with calcium hydroxide in aqueous solution. The result was a clear aqueous solution of calcium polysulfide cherry color with a density of 1.21 g/cm^3. Nanoparticles of sulfur were extracted from calcium polysulfide solution by dilution with water as described in detail in [8]. In laboratory tests we mixed aqueous solution of calcium polysulfide in certain relationships with nutrient medium, as a result of polysulfide molecules decomposed and sulfur nanoparticles appeared in the medium. To field test the aqueous solution of calcium polysulfide in certain ratios mixed with water. In this case also, the molecule of polysulfide decomposed and formed aqueous dispersion containing nanoparticles of sulfur, which is sprayed on plants.

Integral and differential distribution of sulfur particles were measured in water immediately after addition of calcium polysulfide solution in a cell of the analyzer, results are shown in Figure 2 as a marker of the triangle. In this case the size of the sulfur particles are in the range of 10 to 40 nm and the average particle size is 21 nm. The analysis showed that the resulting distribution is not sustainable, and in 10-15 minutes agglomerates consisting of sulfur particles in the range of 140 nm to 400 nm are emerged (show on the figure 2 curves with a marker in the form of unfilled circle (o)). These agglomerates are not sustainable, and under the influence of ultrasound and stirring to break up the original sulfur nanoparticles with an average size of 21 nm.

Along with the measurement of the particle size distribution using a laser particle size analyzer, using Solver Pro M scanning probe microscope, we determined the size and shape of particles of sulfur (see Fig. 3). The data presented in Figure 3 shows that the sulfur nanoparticles are spherical. Using special imaging treatment software, it was established that the particle sizes are in the range of 10 to 50 nm, and the average particle size is 25 nm (shown in Fig. 2), the same as in Figure 2.

Lump sulfur and sulfur in the form of micron powders are known to have an orthorhombic structure. At the same time, the nanoparticles are known to crystallize in the structural state of uncharacteristic macroscopic matter. Therefore, powder of sulfur nanoparticles was analyzed by X-ray diffraction. As a result (see Figure 4), it was found that the sulfur nanoparticles have a orthorhombic structure, which is consistent with previous data of our work [6, 17], and with those of other researchers [2,5].

3.2. Analysis of the antifungal effects of sulfur

We show on (Fig. 5) the data obtained with the use of mycelium snow Schutte. Column diameter snow Schutte for untreated medium is 59 mm (Figure designated as test). For the medium, treated with 2% sulfur dispersion having micrometer dimensions (figure identified as MpS 2%), the column diameter is 47 mm. Thus, treatment of ground sulfur slightly (by 25%) reduced the development of the colony. At the same time, the use of nanoscale 2% sulfur (in the figure labeled as NpS 2%) reduces the diameter of the column 7-fold compared with the untreated sample. If we compare the media containing the same concentration of 2%, it turns out that the nanosized sulfur efficiently micronized sulfur in 5.6 times.

The following (Fig. 6) shows the data obtained with the mycelium of the ordinary Schutte. Here, the diameter of the colony in a cup containing the mycelium in the untreated medium is equal to 60 mm, and in the case of medium containing 2% powdered sulfur micron size diameter of the column is reduced slightly (by 15%) to 52 mm. At the same time, the use of 2% nanoscale sulfur reduces the diameter of the column is 12 times as compared to the untreated sample. Comparison of the results with the use of 2% of nanoscale sulfur with the data obtained with the use of 2% micron sulfur shows that nanoscale sulfur better 10 times. Thus, from Figs 5 and 6 show that in both the ordinary and the snow Schutte using nanoscale sulfur increases the efficiency of the biological effects of sulfur in 7-10 times.

Along with laboratory tests we have conducted field tests as follows. We were prepared by the dispersion of sulfur nanoparticles of different concentrations, which handles the plots of pine seedlings. As a result, we chose the control plots treated with clean water. Feedback sulfur nanoparticles were also compared with the data obtained by treating 2% micronized sulfur. In all cases, sulfur powder mixed with water containing as a surfactant in an amount sulfanol 0.3%. Next (Figure 7) shows the data obtained in the field for different processing conditions. From Figure 7 it is clear that the treatment by dispersion, containing 2% powdered sulfur (2% MpS) led to a reduction in the number of infected plants at 1.32 times, and processing by dispersion containing 2% of nanoscale sulfur (2% NpS) led to a decline of 7.5 times. Figure 7 shows that the use of nanoscale sulfur significantly reduces the number of infected plants, compared with the traditionally used form of micronized sulfur formulation [13,14]. Comparison of the effectiveness of micron and nanoscale sulfur equal 2% concentration shows that the latter is better in 5.7 times. It is also clear that in this case, the effective suppression of fungi is enough to use 1-.2% sulfur dispersion of nanoparticles.

4. Conclusion

Thus, a comparison of laboratory and field experiments show that nanoscale sulfur derived from calcium polysulfide is 5-10 times more effective drug manufactured by ground sulfur. The high efficiency of sulfur nanoparticles due to the high specific surface area, leading to increased efficiency of the biological impact of traditional formulations, as well as a more uniform distribution of the active substance in the laboratory experiments in terms of the test environment, and in the case of field experiments on plant surfaces. The results obtained can be useful for making environmentally safe, effective and cheap fungicide formulations on the basis of nanoscale sulfur.

Acknowledgements

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[14] Specifications 113-04-322-40 Colloid sulfur - paste.

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a b c

Fig. 1. Image of pine branches: a - healthy branches, b - a branch of the affected snow Schutte, c - the branches affected ordinary Schutte

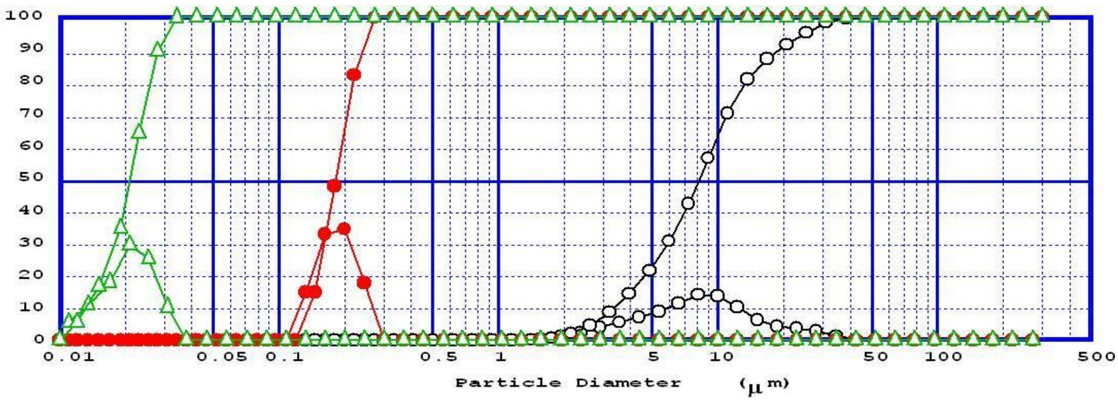

Fig. 2. Integral and differential distribution curves of ground in a roller mill and the resulting release of calcium polysulfide.

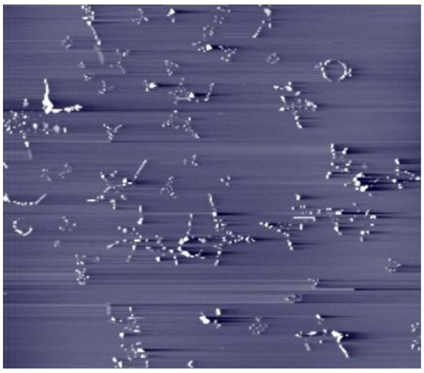

Fig. 3. Image of sulfur particles, obtained using probe microscope

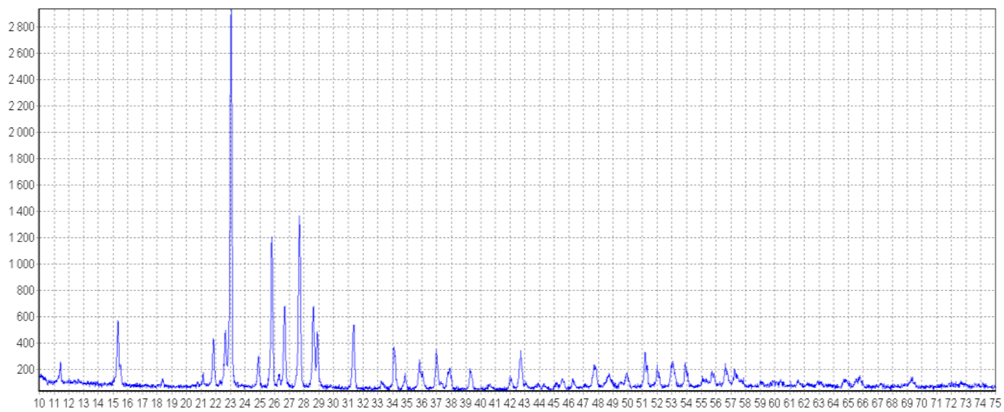

Fig. 4. Diffractogram of sulfur nanoparticles, obtained by using X-ray diffractometer

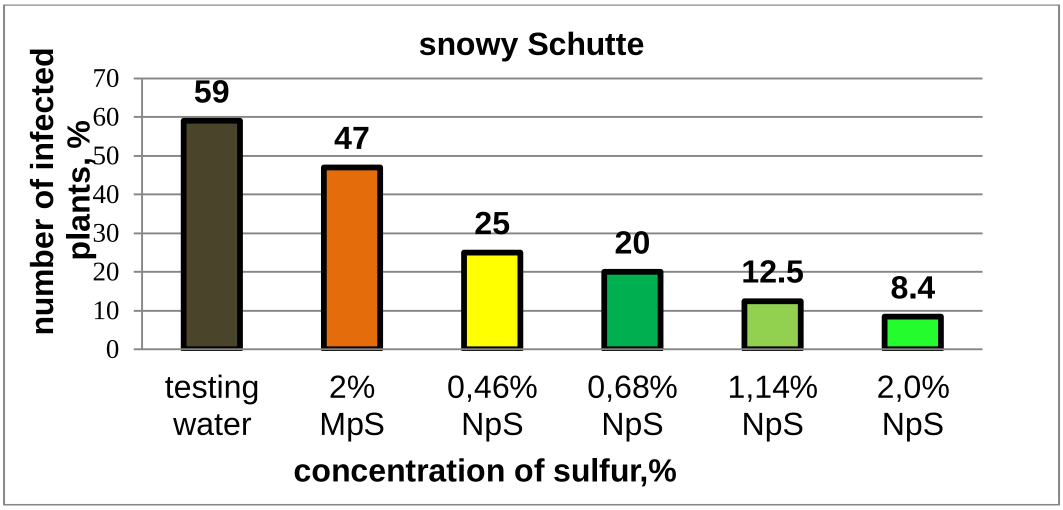

Fig. 5. Biological effects of micronized sulfur particles (MpS) and nanoparticles of different concentrations of sulfur (NpS) on strain Schutte snow fungi. The ordinates are the diameters of the column for different methods of treatment, and control data (testing water) is the result obtained without the use of sulfur.

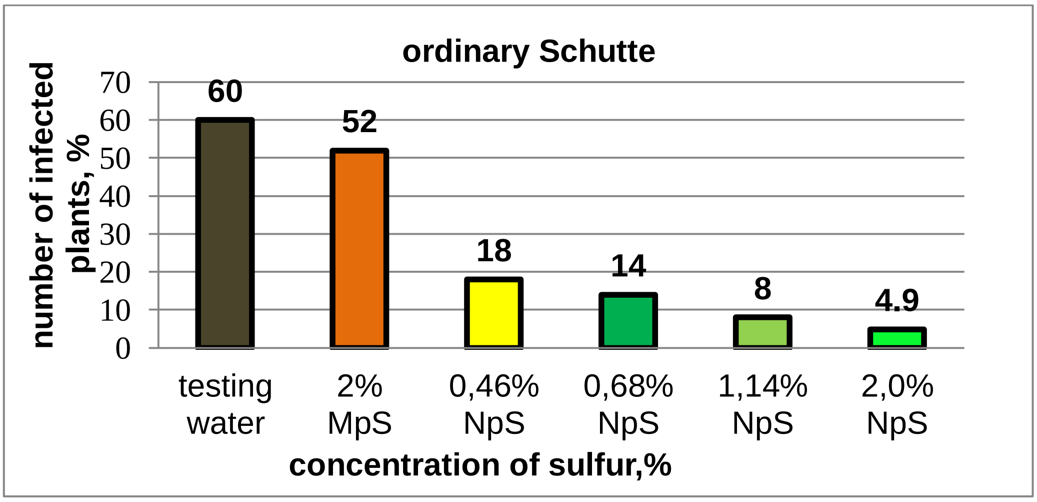

Fig. 6. Biological effects of micronized sulfur particles (MpS) and nanoparticles of different concentrations of sulfur (NpS) on strain Schutte ordinary fungi. The ordinates are the diameters of the column for different methods of treatment, and control data (testing water) is the result obtained without the use of sulfur.

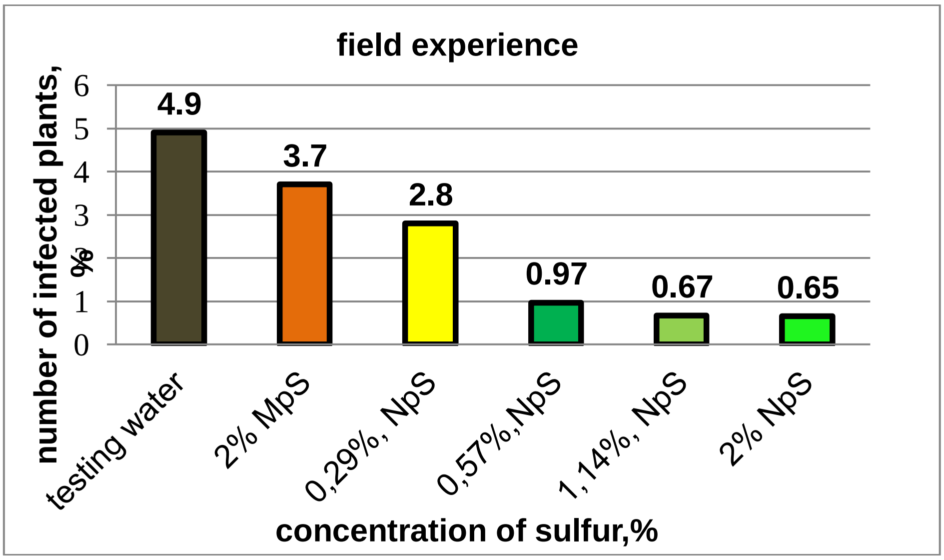

Fig. 7. Antifungal effect of micronized sulfur particles (MpS) and sulfur nanoparticles (NpS), obtained in field experiments.