Biologically Active Substances from Oxidized Lignite of the Itatsky Deposit

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Abstract. Biologically active substances of natural origin are of great interest for agriculture, as their use allows to increase the efficiency of the industry and to obtain environmentally friendly products. The purpose of this work is to determine the biological activity of potassium humates obtained from oxidized brown coal beds of the Itatskoe deposit in the Kansko-Achinsky brown coal basin. Alkaline extraction of potassium humates and study of their biological activity were carried out in laboratories of Kuzbass State Agricultural Academy in 2017-2019. It was found that oxidized brown coals, inferior in their qualities to ordinary ones as fuel, are a promising source of biologically active substances for crop production. The study of biological activity of potassium humates revealed their significant impact on seed germination and morphometric characteristics of cucumber and soybean sprouts. When soaking seeds in solutions of potassium humates with concentrations from 0.001% to 0.1%, small concentrations of humates 0.001% and 0.005% - had the greatest positive effect on the germination and length of soybean roots, length and weight of roots and cucumber stems.

1. Introduction

Research of deep processing products in order to improve their technological characteristics and search for new applications is one of the priority tasks that Kuzbass scientists are currently facing. Brown coals are coals of low metamorphism stage. They consist mainly of recycled parts of higher plant tissues: products of lignin decomposition, cellulose and vegetable protein. Brown coals are characterized by a high content of oxygen, so their specific heat of combustion is the same as that of hard coals and anthracites, so their use as a fuel is limited [10]. The most practically significant product of lignite processing is humic acids and their salts [16].

Humic substances are an integral part of humus and largely determine the fertility of soils [2,4,8]. Brown coals and products of their processing are effective in detoxification of soils from various kinds of pollution [5,6,14].

The Itatskoe deposit belongs to the western part of the Kansk-Achinsk brown coal basin a and is located in the northeast of the Kemerovo region. The Itatsky deposit coal is brown, according to technical classification it belongs to group 2B, subgroup 2: brown vitrified, with prevalence of matte varieties, medium ash, with high sulfur content.

Coal mining is performed by open-pit method with capacity of 300 thousand tons per year. For industrial development, a site with 3.4 mln ton n reserves has been prepared. Coal is used as fuel for municipal needs.

The oxidation zone is widely developed at the layer outcrops under the sediments. The capacity of the oxidation zone varies considerably, reaching 10-12 meters in some sections (15).

Studies by Tomsk scientists showed that the content of more than 20 impurity elements in oxidized coals corresponds to coal Clark. Excess Clark was found for uranium and cobalt. The threshold of "toxicity" is exceeded by one impurity element. These data serve as a refutation of a common myth about high radioactivity of Itathian brown coals. According to the same authors, the average content of humic acids in oxidized coals of the Itatka deposit is up to 60% wt %, which makes them a potential source of water-soluble salts of humic acids - humates [11,1].
Humic preparations on the basis of humates are used as biologically active substances in agriculture, as detoxicants at recultivation of territories polluted with heavy metals, organic substances and oil products, as binders at aggregation of small coal fractions, surfactants in drilling mud [12,13]. Most often, humates are now used in crop production as stimulators of growth or microfertilizer. In contrast to similar synthetic growth regulators, humic preparations influence not only plant metabolism. Their systematic use improves soil structure, its buffer and ion-exchange properties, soil microorganisms become more active. Particular attention should be paid to adaptogenic properties - humic products increase the ability of plants to withstand diseases, drought, overwetting, carry an increased dose of nitrogen salts in the soil. Advantages of humic compounds are also that it increases the absorption of nutrients, and thus reduce the need for mineral fertilizers plants without affecting the harvest and fully comply with the principles of organic farming [2,3,7].

2. Materials and Methods

The article presents the data of the study of properties of brown coals and the obtained and humic preparations obtained in the Kuzbass State Agricultural Academy in 2017-2019. The object of this study were potassium humates obtained from oxidized brown coal beds of the Itatskoye deposit. The subject of the study was the biological activity of potassium humates.

Indicators of quality of ordinary and oxidized in the beds of brown coals were determined in the Test Laboratory of "Kemerovo Center for Coal Expertise" Ltd: total moisture, Wf according to GOST 11014-2001, maximum humidity, Wmax according to GOST 8858-93, ash content, Ad according to GOST R 55661-2013, volatiles yield, Vdaf according to GOST R 55660-2013, mass fraction of total sulfur, Sd according to GOST R 8606-93, heat of combustion is low, Qr according to GOST 147-2013.

To obtain the humates was used the classical method of alkaline extreme (GOST R 54221-2010), in which the process of processing the feedstock (brown coals, peat, sapropel) with an alkaline extractant humic acids are converted into a solution in the form of salts of one-valent cations. According to the same GOST, mass concentration of potassium humates in the obtained solution was estimated and biological activity of the obtained potassium humates was studied [9]. Repetition of the experience is three times analytical. The obtained results are presented in the form of arithmetic averages; reliability of differences in comparison with the control was found by F-criterion at the level of significance 0.05.

3. Results and Discussions

We have compared the data of test reports of ordinary and oxidized brown coals obtained in the Test Laboratory of "Kemerovo Coal Expertise Center" Ltd (Table 1).

| Indices | Unit of measure | Indices values |
|---------|----------------|----------------|
| Total moisture | % | 35.2 | 31.0 |
| Maximum humidity | % | 40.7 | 38.5 |
| Ashes | % | 9.9 | 5.2 |
| Volatile substance yield | % | 46.8 | 24.5 |
| Mass fraction of total sulfur | % | 0.27 | 0.70 |
| Low heat of combustion | Kcal/kg | 3838 15.65 | 2400 9.79 |

The analysis of Table 1 data shows that the combustion heat of oxidized brown coals is higher than that of ordinary 37% and the sulfur content is 159% higher, respectively. Thus, oxidized brown coals, as fuel, are noticeably inferior to ordinary coals in their characteristics, and they should be sought for more worthy use, for example, as a source of biologically active substances.

Grinded brown coal (oxidized or ordinary) of 3 - 500 microns fraction was introduced into diluted solution of potassium hydroxide (ratio of solid and liquid phase 1:10, respectively) and stirred for 2
hours at temperature 80°С. After sedimentation, the liquid phase was separated from the solid phase by decantation.

For estimation of mass concentration of potassium humates in the obtained solution gravimetric method of distillation was used. For this purpose, a pure chemical glass of a 100 ml was placed in a drying cabinet heated to 80 °С and dried to a constant mass. Then 10 ml of potassium humate solution was introduced into the glass with a pipette and evaporated to a constant weight. The difference of masses of pure glass a and glass a with dry residue was taken equal to mass of humates in selected aliquot. As a result, it was found that the mass concentration of potassium humates in solutions is 10.23 and 2.30 % wt. respectively for oxidized and ordinary brown coals. The results obtained allow us to conclude that oxidized brown coals, as compared to ordinary brown coals under these conditions, give a significantly higher yield of the humates.

The biological activity of the obtained potassium humates was studied on cucumber and soybean seeds. The seeds were placed in ten Petri dishes on a cotton cloth wetted with potassium human solutions of different concentrations. Control - water. Data characterizing seed germination are given in graphical form on Figure 1 and 2.

Figure 1 - Soybean seed germination dynamics of SibNIK-315 soybean varieties, depending on the concentration of potassium humates

Figure 1 shows that germinating capacity of soybean seeds on 2-3 days under the action of potassium humate solutions with concentrations of 0.001% and 0.05% n a 40% is higher in comparison with control. At concentrations of 0.01% and 0.1%, germination time was longer and the proportion of germinated seeds decreased. The best soybean seed germination rates were observed at potassium humate concentrations of 0.001% and 0.055%.
Figure 2 - Dynamics of cucumber seeds germination of Obilny variety depending on concentration of potassium humates

The data presented in Fig. 2 show that the greatest positive influence on germination of cucumber seeds was made by solutions of potassium humates with concentration of 0.05% - up to 23%, whereas germination time is prolonged in comparison with control in all variants.

On the ninth day from the beginning of soaking the length and weight of soybean roots were measured (the results in graphic form are presented in Figure 3 and 4).

Figure 3 - Influence of potassium humate concentration on soybean germ root length

As it follows from the graph presented in the picture, 3, potassium humates actively stimulate the development of soybean sprouts in concentrations up to hundredths of a percent. At higher concentrations, the stimulating effect of potassium humates decreases.
The largest increase in the mass of roots was obtained when treated with potassium humates at a concentration of 0.001%. With increasing the concentration of humates, the increase in length and weight of the roots of seedlings slows down.

On the ninth day from soaking was measured the length and mass of the roots and stems of cucumber plants. The results of the measurements are shown in graphical form in Figure 5 and 6.

Figure 4 - Influence of potassium humate concentration on the mass of soybean seedling roots

Figure 5 - Influence of concentration of potassium humates on the length of roots and stems of cucumber seedlings of Obliny variety
Figure 6 - Influence of concentration of potassium humates on the mass of potassium roots and stems of cucumber seedlings of Obilny variety

Analysis of data Fig. 5 and 6 shows that solutions of humates had a significant effect on the skin and development of cucumber plants in all variants. Visually, under the action of small concentrations of humates, cucumber sprouts became shorter, but more massive. Moreover, a noticeable positive effect on weight gain (up to 50%), had concentrations of humates in thousands of percentage points, and at higher concentrations, weight gain decreases and even becomes negative relative to control at a concentration of 0.1%.

The study of biological activity of potassium humates revealed their significant influence on seed germination and morphometric characteristics of cucumber and soybean sprouts. When soaking seeds in potassium humate solutions with concentrations from 0.001% to 0.1%, small concentrations of humates at 0.001% and 0.005% had the greatest positive effect on germination and length of soybean roots, length and weight of cucumber roots and stems. Increase of solutions concentration up to 0.1% leads to suppression of sprouts development. This is consistent with the literature data and has a great practical value. It is possible to obtain up to 10 m³ of working solution from 1 liter of the obtained solution for use in plant growing (seed processing, foliar feeding, irrigation).

Conclusion
It was found out that solutions of potassium humates, obtained by alkaline extreme action from oxidized brown coals of Itatskoye deposit, show biological activity with respect to soybean and cucumber seeds. Large concentrations of potassium humates act as growth inhibitors, while small concentrations have a stimulating effect.

The active growth of the plant in early ontogenesis has a positive effect on further formation of its underground and aboveground organs, and the yield directly depends on the dynamics of photosynthetic apparatus development. Also, as the energy of seed germination increases, the competitive ability of the crop in sowing with weeds increases.

Thus, oxidized brown coals from the Itatskoye deposit, which are significantly inferior to ordinary coals in terms of fuel quality, are the best natural source of valuable biologically active substances, potassium humates, which fully comply with the principles of organic farming. Small concentrations of potassium humates of 0.001% and 0.005% had the greatest positive effect on seed germination and morphometric characteristics of cucumber and soybean germplants.

Organizing the production of humic preparations from oxidized brown coals of the Itatskoye deposit could only significantly increase the efficiency of resource consumption of these minerals, but also contribute to solving such urgent problems for the Kemerovo region as improving the efficiency of reclamation of disturbed lands and obtaining high yields of crops.
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