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### RESEARCH ARTICLE

#### NATURAL NANOMATERIALS – ZEOLITES, AS MELIORANTS OF PETROL-POLLUTED SOILS.

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#### Abstract

Pollution of the soil by petrol is accompanied with a strong negative effect on plants due to changes in its physical-chemical properties, mainly due to an increase in hydrophobicity and the filling of soil capillaries with petrol and the direct toxic effect of petroleum hydrocarbons (phyto toxicity). Zeolite (clinoptilolite), is an ecologically safe effective ameliorant for the reclamation and rehabilitation of polluted soil.

The article presents data on the effect of various concentrations of petrol in the soil on the growth and development of wheat using a zeolite meliorant. It is shown that the introduction of zeolite into petrol-contaminated soil has a significant melioration effect and improves the development of the test culture.

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#### Introduction:-

In recent decades, the already known types of soil degradation (loss of humus, physical degradation, accumulation of pesticide residues and their metabolites) have been accompanied by an extremely dangerous anthropogenic impact factor - petrol pollution. Petrol and petrol products are among the most common pollutants of the environment, causing significant changes in the chemical composition, properties and soil structure; the normal functioning of the soil ecosystem is disrupted for a long time, soil fertility is deteriorating, and the intensity and direction of redox processes are sharply changing [1,2]. The flow of petrol into the soil ambiguously affects the activity of enzymes, which can both increase [3,4] and weaken [5,6,7], depending on the dose and type of pollutant and the type of soil that has been polluted.

Due to the significant intensification of petrol production, losses during transportation and use of petroleum products, the process of alienation of land from economic use is actively taking place. Physical, thermal and chemical methods of purification from petroleum hydrocarbons do not ensure their complete removal from the soil and can be a source of secondary pollution.

Technologies for mobilizing the natural reserves of soil ecosystems aimed at decomposing petrol-pollutants are currently considered as the most promising and effective methods of cleaning. The processes of soil self-purification are largely determined by the functional activity of hydrocarbon-oxidizing microorganisms capable of assimilating petrol as the only carbon source. Therefore, when solving the problem of reclamation of petrol-contaminated soils, it is more expedient to develop ways to stimulate the activity of native petrol-assimilating micro flora of contaminated soil that do not require labor-intensive, expensive operations associated with the isolation, cultivation and

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introduction of hydrocarbon-oxidizing culture of microorganisms. The greatest effect can be achieved through the use of meliorants, for example, zeolites, which provide both sorption of petroleum hydrocarbons and adhesion of petrol-assimilating microorganism cells from the soil [8].

To gathering of petrol and hazardous chemicals from the surfaces, it is enough to introduce zeolite to the affected area and then gather it and utilize. In case of petrol and petrol products, you can simply burn out and reuse.

When restoring soils with a low level of contamination, it is possible to apply zeolite to the affected soil with conventional mineral fertilizer spreaders, after which it can be cultivated and sown with any green (non-food) crop. Zeolite will "pull" pollution from the soil, reliably bind, prevent further spreading (including to groundwater). Thus, in one or two seasons, the soil will be restored.

### Objectives and Methods:-

The purpose of this work was to study the effect of natural zeolite (clinoptilolite), introduced into the petrol-polluted soil, on the growth and development of a test plant. Among the recommended plant species for phytoremediation of petroleum hydrocarbons, representatives of the family of fowl-grass 40 (corn, sorghum, barley, ryegrass, ryegrass, fescue) dominate. Their main advantage is the presence of a well-developed fibrous root system, which forms a large surface area for colonization by soil microorganisms. Legumes are also of interest for use in the phytoremediation of hydrocarbons due to the symbiotic relationship with nitrogen-fixing bacteria. For some of them (alfalfa, fodder beans, peas, clover, sweet clover), a phytoremediation effect was established [9,10].

Phytoremediation was not of our interest, therefore wheat was used as a test plant. It was interesting how this culture would develop under extreme conditions, although it was not ecologically justified sowing grain on contaminated soil. Grains were sown in vegetation vessels, containing up to 3 kg of soil.

Experiment was conducted on a gray-brown soil. The soil was polluted with petrol from the Samgori deposits (Georgia) [11].

Natural zeolite –clinoptilolite containing tuff from the deposit, Khandaki region, Georgia, with a basic mineral content within 70-80%. The experiments were performed in eight variants, each of them in four reiteration.

1. The first variant–clean soil (absolute background).
2. The second variant –soil with a fouling factor of petrol –2.5%.
3. The third variant–soil with a fouling factor of petrol –5%.
4. The fourth variant–soil with a fouling factor of petrol – 10%.
5. The fifth variant–soil + clinoptilolite.
6. The sixth variant–soil + clinoptilolite, fouling factor of petrol – 2,5%.
7. The seventh variant –soil + clinoptilolite, fouling factor of petrol – 5% (substrate).
8. The eighth variant –soil + clinoptilolite, fouling factor of petrol – 10% (substrate).

Before the beginning of the experiment, the sowing qualities of wheat seeds were determined: germinating of seeds (G) and germination energy (GE). Two consecutive sowing was carried out with a one-month break between them. Observations on the productions of each sowing were carried out for 30 days.

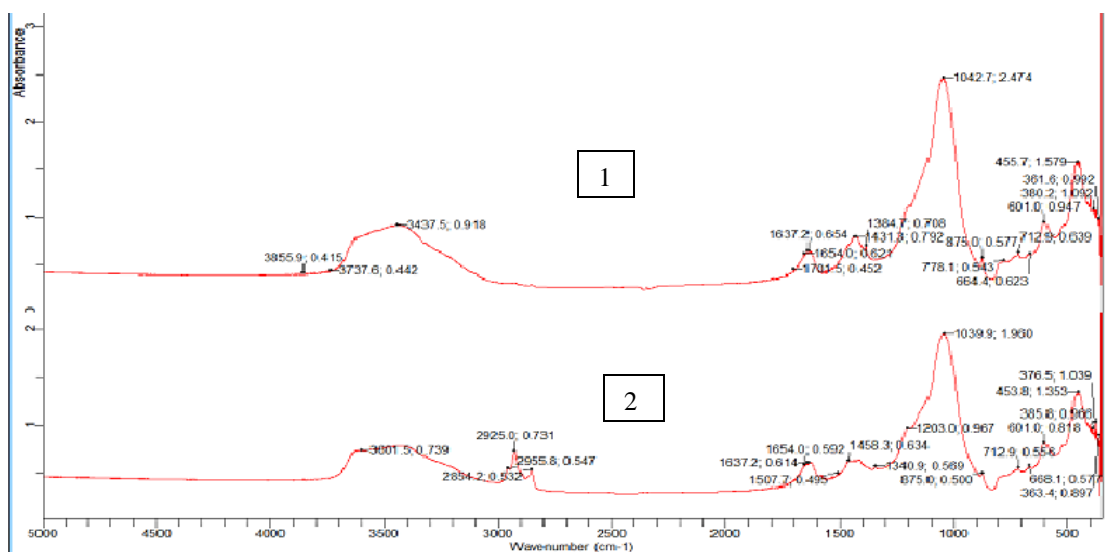
### Results and Discussion:-

Zeolite is a macromolecular system with a developed surface, the activity of which is determined by the molecular-sieve effect of micropores as well as diffusion and sorption processes on the surface, in micropores and channels. These qualities of zeolite stipulate the retention of macromolecular and super molecular structures on the surface of mesopores [12,2]. The popularity of zeolites is explained by the unique physicochemical properties mentioned above. There are a number of problems that can be solved by zeolites, starting with artificial soil on the moon and ending with new medical preparations. Therefore, the famous American scientist F.A.Mampton called zeolites "magic rock" and products of the XXI century civilization [2,13].

Determination of adsorbed petrol products by zeolite is possible using various physical-chemical methods. Infrared spectroscopy is one of the most recognized and reliable method, but this method does not provide an unambiguously complete picture, because at the same wavelength, overlapping absorption bands or vibrations of various organic substances can occur simultaneously and their identification is difficult [14,15].

Infrared spectra were taken in the middle and partly far-infrared regions ( $350\text{--}500\text{ cm}^{-1}$ ) using an Fourier spectrometer of the firm “Agilent Technologies” (Fourier Infrared Spectrometer Cary 630 FIJR). A detailed analysis of the infrared spectra showed that the spectrum consists mainly of two parts: the far and, in part, the middle infrared region, typical for zeolite frame, both deformational and valency vibrations of  $1200\text{--}350\text{ cm}^{-1}$  [16,17,18]. The other vibration bands mainly belong to organic matter and water, and are located in the interval  $1300\text{--}3650\text{ cm}^{-1}$  [19] (Fig. 1).

**Figure 1:** IR spectra of the initial natural clinoptilolite (1) and natural clinoptilolite with adsorbed petroleum products (2).



Of particular interest are the two spectral regions  $2854\text{--}2955\text{ cm}^{-1}$  and  $1507\text{--}1340\text{ cm}^{-1}$ . The region of  $2800\text{--}300\text{ cm}^{-1}$  corresponds to extreme hydrocarbons [14]. According to the experimental results, the obtained bands of  $2854$ ,  $2925$  and  $2955\text{ cm}^{-1}$  can theoretically be attributed to symmetric deformation vibrations of the methyl group  $\text{--CH}_3$   $2872\text{ cm}^{-1}$  and  $2926\text{ cm}^{-1}$ , as well as symmetrical  $2853\text{ cm}^{-1}$  and asymmetric  $2926\text{ cm}^{-1}$  vibrations of the methylene group  $\text{--CH}_2$  [14,20]. The low intensity bands of  $1340$ ,  $1458$  and  $1507\text{ cm}^{-1}$  can be attributed to the deformation vibrations of the above groups. Judging by the intensity of the peaks, the concentration of hydrocarbons of the methylene group exceeds the concentration of hydrocarbons of the methyl group.

It should be noted that the content of alkenes and alkanes in the petrol of the Samgori deposit (Georgia) prevails over the content of aromatic hydrocarbons [21]. Due to the size of pores on the surface of the zeolite, adsorption of alkanes and alkenes may occur much more easily than adsorption of aromatic hydrocarbons (Fig. 1).

Under laboratory conditions, experiments were conducted to study the effect of petroleum products and zeolites on laboratory germinating power, germination energy, and the formation of wheat vegetative mass. Table 1 shows the averaging data of the first and second sowing of the following biometric parameters of the test culture: germination energy (GE), germinating of seeds (G). The response of plants to soil pollution by petrol was estimated visually during the vegetation process. The introduction of zeolite has a meliorative effect and improves characteristics compared with variants with petrol-polluted soil. Further analysis suggests a decrease in the phyto toxicity of contaminated soil over time and the optimization of its properties for growing wheat.

**Table 1:** Biometric characteristics of the test culture

	Sowing	Test samples							
		1	2	3	4	5	6	7	8
Germination Energy	1 <sup>st</sup> sowing	80	-	-	-	80	20	10	30
	2 <sup>nd</sup> sowing	100	50	10	-	100	50	-	-

Germinating power	1 <sup>st</sup> sowing	80	-	-	-	90	60	60	60
	2 <sup>nd</sup> sowing	100	80	20	-	100	80	70	10

Analysis of the tabular data of the first and second sowing shows that the introduction of zeolite on petrol-contaminated soil has a significant meliorative effect and a beneficial effect on the germination energy and germinating power of plants. Pollution of the soil by petrol is accompanied with a strong negative effect on plants due to changes in its physical-chemical properties, mainly due to an increase in hydrophobicity and the filling of soil capillaries with petrol and the direct toxic effect of petroleum hydrocarbons (phyto toxicity). The germination energy on the substrate increases by 10-30% at the first sowing, and germinating power by 60% for the first variant and by 10-50% for the second variant on the substrate contaminated with 2.5, 5-10% petrol. The data given in Table 1 were calculated on the fourth (GE) and on the tenth (G) day after sowing.

### Conclusion:-

Thus, the experimental data have shown that the zeolite (in our case—clinoptilolite), is an ecologically safe effective ameliorant for the reclamation and rehabilitation of polluted soil. The results require further extended research.

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