INVESTIGATION OF THE INFLUENCE OF THE QUALITY OF SOILS IN THE DEVELOPMENT OF PLANTS WITH THE HELP OF THE METHOD OF IR-SPECTROSCOPY

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The paper presents the data of spectral analysis of samples of test plants grown on contaminated soils with admixtures of natural sorbents. It is shown that the introduction of zeolites and schungites allows to clean the soil from ions of heavy metals and oil products. Using method of multiple frustrated total internal reflection in the range of 1800-1200 cm^{-1} without the polarization of the light flow and in parallel and perpendicular polarized light spectrums of the external structures and cells of plant objects are obtained, dichroisms of absorption bands are defined.

It is established that the introduction of sorbents in soil increases the productivity of the soil, exerting a positive influence on the development of plants. With the use of IR-spectroscopy it is determined that presence of zeolite in the soil increases the adaptive properties of plants to the environment.

PLANT OBJECTS, SORBENTS, OPTICAL METHODS

INTRODUCTION

Due to the constant development of megalopolises and widening pollution of the environment the threat to the stability of city ecosystems has arisen. Not only the majority of vegetation and wildlife types but soils that are integral to city ecosystems are affected negatively by urbanization as well. In recent years the problem of the degradation of city soil cover had been acknowledged, evaluation of ecological harm to the environment by the destruction of soil cover had been payed attention to. Under city conditions special kind of anthropogenically modified soils – urbanozems – are formed, their properties differing significantly from zonal soils. As a rule those differences are of adverse or in the best case scenario neutral nature to the growth of majority of plant types. Negative influence of city conditions on green spaces manifests through soils properties changes, atmosphere and subsoil water pollution, increased level of noise and mechanical damage.

Various methods are used to raise the quality of contaminated soils. One of those methods is the introduction natural sorbents – zeolites and shungites – into urbanozems. These sorbents are able to absorb the most frequently encountered city soil toxicants – heavy metals and oil products. [1, 2, 3, 4] Soils biotesting for quality assessment method is widely known [5], it is based on test plants germination speed and biomass quantity evaluation. It is shown in work [6] , that objective data regarding soils purification by the use of sorbents can be acquired based on the survey of the test plant living cells properties gradient by internal reflection spectroscopy method.

The determination of sorbent type that affects the development of plants in the best way by the use of aforementioned method is presented in this work.

RESEARCH METHODS AND RESULTS

The Maksovskoe field shungite and Kholinskoe field zeolite of 0,1-0,7 mm fraction were used for the experiment. Contaminated soils, samples of which had been taken by envelope method on the territories of Dzerzhinsky, Moscow Oblast along city highways on the distance no more than 3m from roadbed from the depth of 0-20cm served as objects of research.

Individual probes of urbanozems had zeolite and shungite in quantities of 5% of mass added to them and then the biotesting of original soils and resulting soil substrates has been conducted. Cress served as test plant.

The presence of mobile forms of heavy metals in soil samples prior to and after 2 weeks of contact with sorbents has been analyzed by atomic absorption spectroscopy method, the presence of oil products - using analyzer "Fluorat-02-3M". Soil samples water extract pH changes and presence of organic compounds' carbon in them have been simultaneously monitored by photometry method.

The properties of cells of test plants that were raised on examined original and sorbent treated soils had been inspected using internal reflection spectroscopy utilizing IKS-29 unit.

Works [6, 7] show, that the use of spectral method of multiple frustrated total internal reflection for noninvasive examination of living cells with the use of polarized light in IR band allows to determine biopolymer molecules chemical bonds spatial organization (order) level change. Entropy reduction which showcases ecosystem's welfare is expressed through the rise of structuredness of cell spatial organization and cell biochemical components' molecular structure dichroism.

The MFTIR (multiple frustrated total internal reflection) method is based on the phenomenon of electromagnetic radiation penetration from more optically dense to less optically dense environment when angle of drop $\theta < \theta_{cr}$, where

$$\theta_{cr} = \arcsin\left(\frac{n_1}{n_2}\right)$$, where

n_1 - measuring element refractive index (more optically dense environment),

n_2 - studied object refractive index (less optically dense environment).

Given method allows the analysis of multi-component, heterogeneous, highly dispersive and even opaque substances. Analyzed substance is applied on measuring element which is then installed into attachment which is then installed into IR spectrometer sample compartment. After attachment's adjustment the sample's spectrum is recorded. As a rule no special preparation of the sample is required for spectrum obtainment. It is possible to conduct quantitative analysis based on absorption band when building a calibration line. Decryption of chemical bonds is possible with the use of characteristic group frequencies' summary scheme.

It is known that with the optimal choice of spectrum obtainment conditions experimentally defined MFTIR absorption band intensity is connected with the examined substance quantity by following relation:

$- \ln R = \alpha N d_{ef} = \varepsilon C N d_{ef}$,

where α — substance absorption index, cm^{-1};

ε — substance absorption molar coefficient when in transparent solvent, l/cm·mole;

C - density, mole/l;

R - experiment measured reflection coefficient;

d_{ef} — investigated sample effective thickness, cm;

N — number of reflections.

In turn effective thickness depends on electric field amplitude perturbation on different refraction index environments' border. For a massive sample the thickness of which is many times bigger than damped field penetration depth in the case of flat polarized light for perpendicular and parallel components we have:

$d_{ef\perp} = 2d_p \cdot \cos\theta/(1 - n_{21})$,

$d_{ef\parallel} = d_{ef\perp} \{(2\sin^2\theta - n_{21})/[(1 + n_{21})\sin^2\theta - n_{21}]\} d_p$,

where $n_{21} = n_2 / n_1$ — relative refraction index,

n_2 - substance refraction index (in case of absorption reflection and refraction indexes are connected by the following relation $n_2 = n_1 - ik_2$),

n_1 — MFTIR measuring element material refraction index,

θ - angle of incidence,

d_p - damped field penetration depth.

The study of cells' individual components' molecules' orientation on measuring element's surface can be done by analyzing MFTIR spectrum absorption band intensity acquired with varying polarization of flat polarized light for one of θ angles. It's most convenient to analyze with $\theta = 45^o$, because with that in case of isotropic distribution of molecules $2d_{ef\perp} = d_{ef\parallel}$, and mean value of $d_{ef} = (d_{ef\perp} + d_{ef}/(_{\parallel}2$ approximately equals d_p.

The $d_{ef\parallel\perp}$ evaluation can also be conducted based on samples' optic density utilizing formula:

$D_{\parallel\perp} = -\lg R_{\parallel\perp}^N = \alpha \cdot N \cdot d_{ef\parallel\perp}$.

This leads to the conclusion that change of effective thickness $d_{ef\parallel\perp}$ can be judged based on change of optical density $D_{\parallel\perp}$ with varying direction of polarization of light source.

It is necessary to make sure that the last formula is true for chosen experiment conditions prior to the conduction of the experiment. The use of this formula significantly facilitates analytical part of work, as it allows to utilize linear relation between D and d_{ef}.

The evaluation of structural organization order is conducted through calculation of examined plant object's biopolymer spectrum's optical indexes (dichroic relations) utilizing baseline method. [7]

Measurement method. Plant object sample had been placed on measuring element, plant object's outer structures and cells spectrum had been taken in 1800-1200 cm^{-1} range without polarization of light stream, then in parallel and perpendicular polarized light. KO2 measuring element made out of zinc sulfide had been used to acquire the spectrum of outer structures, germanium based measuring element had been used for inner cells spectrum acquisition.

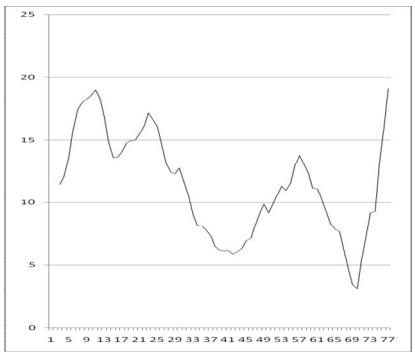
Results of the experiments showed that:

- natural sorbents – shungite and zeolite – can change polluted soil composition on contact (clean it) from pollutants of organic and inorganic nature, decreasing the amount of heavy metals (zinc, lead and cadmium) by 85-100% and oil products by 70-100%.
- acidity of soils can be regulated with natural sorbents: pH can be moved to acid side by introducing shungites, alkaline - zeolites;
- natural sorbents change the level of organic carbon in soils insignificantly;
- the productivity of test plant biomass in all cases of soils with sorbent admixtures was higher than in original soils;
- clear mechanisms of soil contents impact on plants development are hard to identify by biotesting.

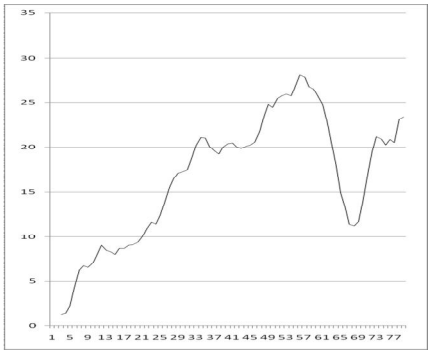
With the purpose of acquiring more detailed data regarding sorbents (shungite, zeolite) impact on plant development plant samples spectrums had been acquired from plants raised on soil samples with admixtures of shungite and zeolite utilizing the above-stated method.

Plant samples (outer structures and inner layers of cells) spectrums had been acquired without polarization and in parallel and perpendicular polarized light. (pic.1-12) The intensity (presence) of absorption bands in ranges of 1730 cm^{-1}, 1650 - 1620cm^{-1} and 1550 cm^{-1}, characteristic of lipids, amide -1 (C – O bond) and amid – 2 (N – H bond) respectively had been compared for all retrieved spectrums. Mentioned substances define the synthesis of proteins that are vital for cells.

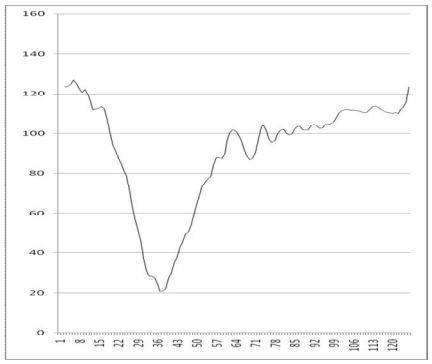
Picture 1.Cress cell outer structures no polarization spectrum (zeolite)



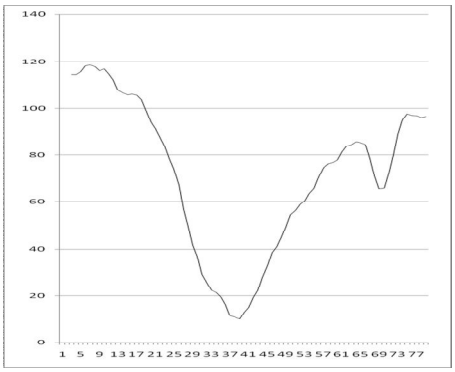
Picture 2. Cress cell outer structures parallel polarization spectrum (zeolite)



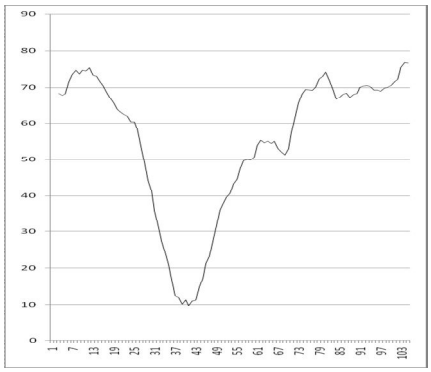
Picture 3. Cress cell outer structures perpendicular polarization spectrum (zeolite)



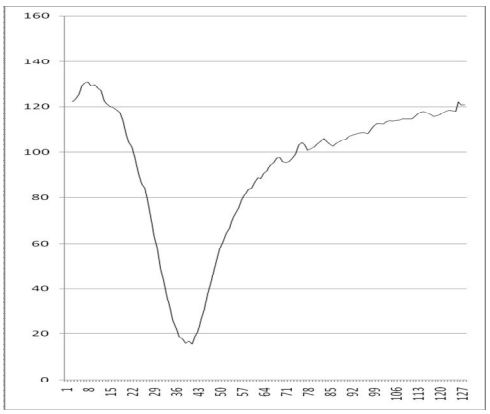
Picture 4.Whole cress cell no polarization spectrum (zeolite)



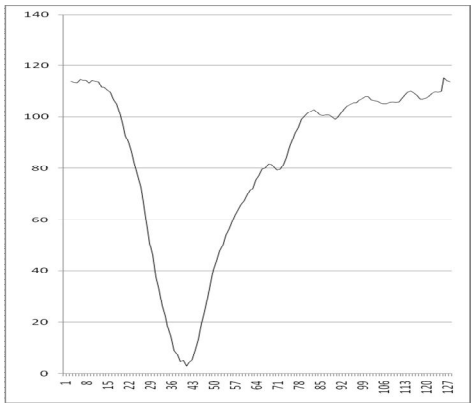
Picture 5. Whole cress cell parallel polarization spectrum (zeolite)



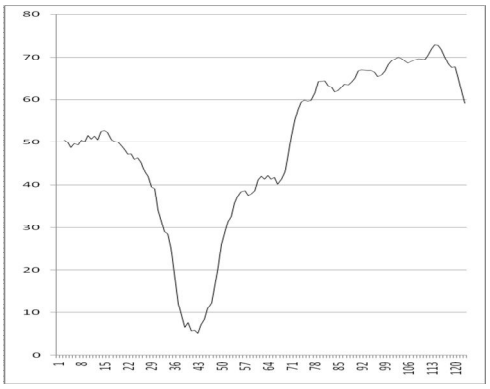
Picture 6. Whole cress cell perpendicular polarization spectrum (zeolite)



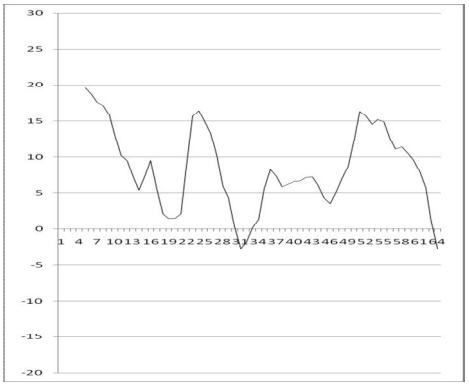
Picture 7. Whole cress cell no polarization spectrum (shungite)



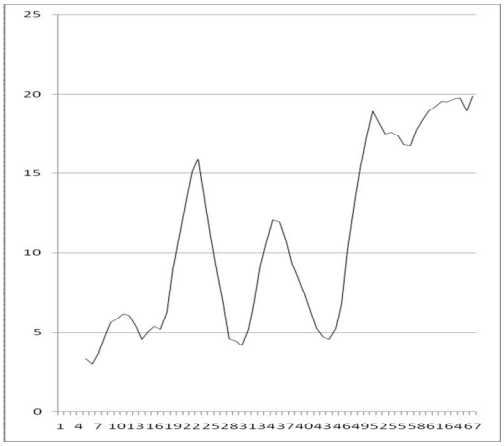
Picture 8. Whole cress cell parallel polarization spectrum (shungite)



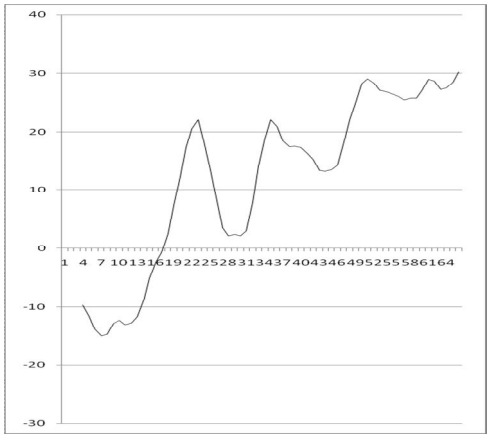
Picture 9. Whole cress cell perpendicular structures no polarization spectrum (shungite)



Picture 10. Cress cell outer polarization spectrum (shungite)



Picture 11. Cress cell outer structures parallel polarization spectrum (shungite)



Picture 12. Cress cell outer perpendicular polarization spectrum (shungite)

Examined samples optical densities and those densities dichroic relations had been calculated for aforementioned absorption bands based on obtained spectrums. Then dichroic relations differences had been determined utilizing method outlined in work [7]. The results are as follows:

Chart1. Examined soil samples dichroic relations differences

Soil sample characterization	Dichroic relations difference
soil sample №1 with 5% mass shungite admixture, contact time 14 days	0,04
soil sample №1 with 5% mass zeolite admixture, contact time 14 days	0,45
soil sample №2 with 5% mass shungite	0,03

admixture, contact time 14 days	
soil sample №2 with 5% mass zeolite admixture, contact time 14 days	0,25

According to statements outlined in work [7] by Koroleva S., living organisms among them plants that adapt to environment in the best way possible, meaning, they possess a favorable state, are characterized by notable differences in cells' outer structures and inner layers biopolymer molecules chemical bonds spatial organization (order) degree, namely, by bigger dichroic relations difference. Therefore data presented above showcases that addition of zeolite to soil does not only provide it's purification from various substances (heavy metals, oil products) but also creates better conditions for plants development compared to shungite.

CONCLUSION

Thus, with the help of soil samples biotesting it is established that natural sorbents shungite and zeolite introduction into polluted soils facilitates plant growth due to absorption of toxicants (mobile forms of heavy metal ions and oil products) from the them. In addition, it is shown that IR range FTIR method test plant cells study allows to estimate soil contents impact on plants' development. It is determined that zeolite's presence in soil raises plants environment adaptive capabilities compared to the use of shungite.

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