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Fourier transform infrared spectroscopic analysis of mine remediation soil

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Изследване на рекултивирана минна почва чрез инфрачервена спектроскопия с Фурие преобразуване

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Abstract. Mine soil reclamation analysis is important because it helps characterize the chemical composition of mine soil. Fourier transform infrared analysis provides valuable insight into the chemical composition, contaminant content and overall quality of mine soil, enabling informed decision-making and effective reclamation practices. It was investigated reclaimed mine soil in Bulgaria was analysed. The aim is to analyse the soil quality and obtain more comprehensive information for future monitoring. There is a common class of soil minerals, namely carbonates, which reduce the mobility of metals. Anthropogenic contaminants such as alkanes and aromatic compounds, which are toxic and could potentially contaminate groundwater or affect the health of organisms in the ecosystem. Fourier transform infrared spectra for iron metal oxides have been found to be key indicators of pedogenic processes such as weathering and strongly influence soil colour as well as retention of ions and anthropogenic compounds.

Keywords: Fourier transform infrared analysis, mine remediation soil.

Introduction

Performing Fourier transform infrared (FTIR) analysis for mine soil reclamation is important because it helps characterize the chemical composition of mine soil. It provides information about the presence of different compounds, functional groups and minerals in the soil (Geoffrey, 2007). This knowledge is crucial for understanding the properties of the soil and the potential limitations for reclamation. In this way, the presence of contaminants in the mine soil, such as heavy metals (Dong, 2021) or organic pollutants, can be detected (Palanivel, 2020). By detecting and quantifying these contaminants, appropriate remediation strategies can be developed to ensure safe and effective reclamation of the soil. Evaluation of soil quality is very important and can be done by assessing the organic matter content, nutrient availability and overall health of the soil (Bünemann, 2018). This information helps determine the suitability of the soil for plant growth and ecosystem restoration. The data obtained from the FTIR analysis helps formulate reclamation plans tailored to the specific needs of the mine soil (Larney, 2012). It helps in the selection of suitable amendments, soil additives and vegetation types that can improve the fertility, structure and stability of the soil. This is a monitoring tool during the reclamation process. By regularly analysing the soil, changes in its composition and quality can be tracked so that reclamation strategies can be adjusted if necessary.

The aim is to use FTIR analysis to identify various organic and inorganic compounds in the soil,

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such as minerals, organic matter and contaminants, which will help in the assessment of soil quality and enable informed decisions for agricultural practices, environmental management and land use planning as well as to provide more comprehensive information for future monitoring of reclaimed mining soils in Bulgaria.

Materials and methods

The samples were taken from tailings dams, which are a consequence of the activities of a leading company in the mining industry in Bulgaria. The object is divided into two sub-objects and covers the reclamation of about 2500 acres. The tailings dam 1 has a volume of 150 million tons; it is closed and reclaimed and sampled (B1-1, B1-2, B1-3, B1-4, B1-5).

FTIR spectroscopy is used to detect changes of major functional groups in molecules that vibrate when irradiated with light of specific wavelengths. These vibrations and their intensity are plotted against the frequency of the light (cm^{-1}) to which the sample is exposed to generate an FTIR spectrum. It was performed with an FTIR spectrometer, Varian 660-IR, Austria, 2009; KBr pellets. The FTIR model used, the peaks in the 4000–400 cm^{-1} range and acquired with the use of 4 cm^{-1} resolution yielding. Deviation in glass density, molar absorptivity, and sample thickness typically result in ± 10% total deviation. All samples were finely ground and dried at 39 °C for 48 hours before recording the FTIR spectra. In the next step the sample is ground with KBr to obtain a homogeneous KBr pellet for scanning. The concentration of the sample in KBr should be in the range of 0.2% to 1%.

Result and discussion

Fourier Transform Infrared Spectroscopy measures the absorption and transmission of infrared light by the soil sample. It provides information about the functional groups present in organic and inorganic compounds, allowing for the identification and quantification of various soil components. This type of analysis provides valuable information on the chemical, physical and biological properties of the soil, which is crucial for assessing the effectiveness of remediation measures and understanding the potential for ecosystem recovery. The results of the analyzes are shown in Table 1.

The components $Ca(OH)_2$ and $Mg(OH)_2$ are available in all samples characterized in the range 3623–3692 cm^{-1}. $Ca(OH)_2$ reduces the mobility of the metals and the phytostability and also reduces the absorption of the metals by the plants. The absorption bands in the range 3418–3428 cm^{-1} are typical for bound and unbound hydroxyl groups and H_2O molecules. The absorption bands in the range 2879–2877 cm^{-1} are typical of alkanes, a type

Table 1. Fourier transform infrared spectroscopy of mine remediation soil

No	Wavenumber/ cm^{-1}					Vibration band	Compounds
	B1-1	B1-2	B1-3	B1-4	B1-5		
1.	3691 3623	3692 3623	3692 3623	3692 3623	 3623	ν (Ca-O) ν (Mg-O)	$Ca(OH)_2$, $Mg(OH)_2$ (Coates, 2000)
2.	3427	3428	3427	3418	3427	ν_s (O-H)	absorbed water (Derrik, 1999), (Davis, 2002)
3.	2879	2878	2879	2879	2877	ν_s (C-H)	alkanes (Hesse, 1987), (Keri, 2012), (Keiluweit, 2010)
4.	1632	1632	1632	1632	1621	ν_s (C=C)	amides (Hesse, 1987), (Keri, 2012), (Keiluweit, 2010)
5.	1029	1009	1029	1026	1029	ν_{as} (Si-O-Si)	organic silicon in Oxy compounds (Margenot, 2017)
6.	777	777	760 778	758 777	776	δ_s C-H	aromatic compounds, (Nakamoto, 2009)
7.	692	692 646	692	692	693 645	ν_s Fe-O	hematite α-Fe_2O_3, FeO_6, (Margenot, 2017)
8.	531	531	531	531	531	ν_s Fe-O-(H)	Fe-O-(H) (Margenot, 2017)
9.	468	466	469	469	465	δ_{as} (O-Si-O)	quartz SiO_2 (Ouatmane, 2000). (Lee, 1986)
10.	430	431	430	–	428	δ_s (O-P-O)	PO_4^{3-} in phospates (Griffiths, 1985), (Smith, 1995)

of hydrocarbon compound that can occur in soil. They are organic molecules consisting exclusively of carbon and hydrogen atoms and are arranged in a linear or branched chain structure. Alkanes can originate from various sources, including natural processes such as the decomposition of organic matter or the release of hydrocarbons by plants and microorganisms. In addition, human activities such as the use of fossil fuels or the release of industrial waste can also introduce alkanes into the soil. The presence of alkanes in soil can have an impact on the environment, as some alkanes are toxic and can potentially contaminate groundwater or affect the health of organisms in the ecosystem. Monitoring and controlling alkane levels in soil is important for maintaining environmental quality. The presence of a band at 1632–1621 cm^{-1} can be a measure of soil hydrophobicity, which corresponds to soil wettability (Margenot, 2017). The ratio of aliphatic C-H stretching at 2879–2877 cm^{-1} relative to aromatic C=C stretching at 1632–1621 cm^{-1} has been used as an index of humification (Tan, 2003). Phyllosilicates are the most abundant class of soil minerals. These minerals consist of Al in octahedral coordination with O(H) bound to Si films in tetrahedral coordination with O. The sensitivity of FTIR absorption to these bond types, their coordination and other features of the mineral structure enables the identification of phyllosilicates of the structural class 2:1 phyllosilicate (e.g., nacrite) (Margenot, 2017). This is because 2:1-layer silicates exhibit a single broad absorption peak at 1029–1009 cm^{-1}. Phyllosilicates are a type of clay mineral characterized by their layered structure and the presence of silicate plates. Phyllosilicates refer to their ability to attract and retain cations (positively charged ions) in the soil. Thanks to this property, phyllosilicates can retain important plant nutrients such as potassium, calcium and magnesium, preventing their leaching and making them available for plant uptake. They contribute to soil aggregation and the formation of stable soil aggregates. These aggregates improve soil structure, porosity and water infiltration, promote root growth and improve the soil's ability to store water. Phyllosilicates also have the ability to hold water in their interstitial spaces, providing a moisture reservoir for plants. Phyllosilicates can serve as a source or sink for various nutrients in the soil. They can adsorb and release nutrients and thus influence their availability to plants. Phyllosilicates can also facilitate the weathering of primary minerals, releasing essential nutrients over time. The absorption bands in the range 777–760 cm^{-1} could be assigned to arene compounds, which are also known as aromatic hydrocarbons and occur in soils. Arenes are organic compounds that contain a ring of carbon atoms with alternating single and double bonds, known as an aromatic ring. They are commonly found in petroleum products, such as gasoline, as well as various industrial chemicals and pollutants. Arene compounds can enter the soil in a variety of ways, such as spills, leaks or improper disposal of these substances. Once in the soil, arenes can persist and potentially have a negative impact on soil quality and the surrounding environment. The presence of arenes in soil can affect soil microbial activity, plant growth and the overall health of the ecosystem. Monitoring and controlling arena levels in soil is important for environmental protection and soil remediation. The main absorption in the FTIR spectra in the 500–400 cm^{-1} range can be attributed to hematite (α-Fe_2O_3). Other oxides present in the soil are ferrihydrite, lepidocrocite, maghemite, magnetite and schwertmannite. These metal oxides are important indicators of pedogenic processes such as weathering and have a strong influence on soil colour and the retention of ions and anthropogenic compounds. Iron oxides in soil contribute to various soil properties and processes. They can improve soil fertility by providing plants with important nutrients such as iron. Iron oxides can also influence soil structure, water holding capacity and nutrient retention. They also play a role in the adsorption and release of other elements and compounds in the soil.

Conclusion

In the conducted FTIR analysis of reclamation mine soil identifies various organic compounds in the soil, including humic substances, organic matter, and contaminants. This information helps to assess soil quality, understand nutrient cycling and monitor contaminants. Calcium and magnesium ions play a role in soil aggregation and stability. In this soil they can promote the formation of stable soil aggregates, improve soil structure and reduce problems such as compaction and erosion. Due to the presence of aliphatic and aromatic stretching bonds, it can be judged as a process of humification. This is a good assessment that the reclamation is positive and successful. Anthropogenic contaminants were detected such as alkanes and aromatic compounds, which are toxic and could potentially contaminate groundwater or affect the health of organisms in the ecosystem. It is suggested the application of treatment methods such as bioremediation, activated carbon adsorption and soil vapor extraction could be applied. Phyllosilicates are involved in various chemical reactions in the soil, including ion exchange, complex formation and catalysis. These reactions influence nutrient cycling, soil pH and the transformation of organic matter, which ultimately has a positive effect on soil fertility and nutrient availability. The main catalyst for Fe(II) oxidation is native iron oxide, which also makes sure that the crystallinity and composition of the newly created minerals are similar to those of the parent minerals. There are crystalline iron oxides in this soil. Repetitive Fe(II) oxidation and its precipitation is probably going to cause highly crystalline phases to accumulate, whereas Fe(II) oxidation is probably going to be slower and produce more Fe(III) phases. Given that iron oxides range significantly in their capacity to engage in surface absorption and electron transfer activities, these variables are also anticipated to have an impact on the dynamics of carbon, nutrients, and pollutants in soils.

The reclamation was carried out qualitatively and the actions taken were effective. It is necessary to carry out monitoring and tracking of indicators over a certain period of time to confirm sustainable positive practices.

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