International Journal of Advanced Research in Science, Engineering and Technology

ISSN: 2350-0328

Vol. 12, Issue 7, July 2025

Characterization of an Organomineral Material Based on Sludge Phosphorite and Humic Acid Using Structural and Phase Analysis Methods

Ruziyeva Ruxsora Suratillo qizi , Isomurodova Sabina Yoqin qizi , Temirov Uktam Shavkatovich , Usanbayev Najimuddin Halmurzaevich

Basic doctoral student, Navoi State Mining and Technology University
Student of Navoi State Mining and Technology University
Professor, Navoi State Mining and Technology University,
Deputy Director for Scientific Work, Institute of General and Inorganic Chemistry of the Academy of Sciences of Uzbekistan

ABSTRACT: This study investigates the structural and phase characteristics of an organo-mineral material prepared from phosphorite sludge and humic acid using infrared (IR) spectroscopy and X-ray diffraction (XRD) analysis methods. The IR and XRD results reveal strong interactions between humic substances and phosphate phases, including covalent and ionic bonding, the formation of bioavailable phosphorus compounds, and the occurrence of decarbonation and oxidation processes. The material exhibits a high density of active functional groups, structural stability, and significant agronomic potential. These findings confirm the feasibility of using the synthesized material as both an effective fertilizer and a potential adsorbent for environmental remediation applications.

KEYWORDS: phosphorite sludge, humic acid, organo-mineral material, infrared spectroscopy, X-ray diffraction analysis, phosphate compounds, fertilizer, adsorption.

I.INTRODUCTION

In modern agriculture, the issues of fertilizer efficiency and environmental safety have become globally significant. Conventional mineral fertilizers, though effective in increasing crop yields, are not only economically expensive but also contribute to the rapid depletion of natural resources and ecological imbalance. In this context, the development of high-value organo-mineral fertilizers based on renewable resources—particularly phosphorite sludge, considered as an industrial waste, and naturally occurring humic acids—holds considerable scientific and practical importance[1].

Organo-mineral fertilizers are substances composed of both organic and mineral components, and their agronomic performance and ecotoxicological safety are evaluated using a variety of analytical techniques. Among these, infrared (IR) spectroscopy and X-ray diffraction (XRD) analysis are essential tools for investigating the structural and phase composition of materials prepared from phosphorite sludge and humic acids. These techniques provide valuable information on crystallinity, bonding states, active sites, and the mineralogical composition of the materials[2].

Several studies have confirmed the potential of major phosphate compounds found in phosphorite sludge (e.g., $Ca_3(PO_4)_2$, $Ca_5(PO_4)_3OH$) as phosphorus sources for agricultural use. However, their direct bioavailability is limited, which can be significantly enhanced by complexation with humic acids. For instance, Visentsev et al. (2018) experimentally demonstrated that such humic–phosphorite composites exhibit high adsorption capacity and improved phosphate ion mobility[3].

Humic acids are natural products of the decomposition of organic matter and are characterized by a polyfunctional structure rich in carboxylic, phenolic, and ketonic groups. These functional groups actively participate in ion exchange, metal chelation, and adsorption processes. Several researchers have emphasized the role of humic substances in the adsorption of metal ions when combined with carbon structures. When humic substances interact with phosphorite sludge, they form organo-mineral complexes whose characteristics can be effectively evaluated using IR spectroscopy[4].

Infrared spectroscopy is a powerful tool for identifying the functional groups present in a substance. Vibrations in the 1700–1500 cm^{-1} range, associated with carboxyl and carbonate groups, indicate the formation of chemical bonds between humic acids and phosphorite. Analytical reports (2018) have noted the ability of –COOH groups in humic acids to interact with Ca^{2+} ions, forming partially or fully neutralized complexes[5].

XRD analysis is also widely employed to characterize the mineral composition of phosphorite sludge. In studies of composite sorbents based on bentonite and hydroxyapatite, XRD has proven useful in distinguishing between amorphous and crystalline phases of phosphates. The interaction of phosphate compounds with humic acids may result in the formation of $Ca(H_2PO_4)_2$, $CaHPO_4$, and hydroxyapatite phases, which are more bioavailable and therefore agronomically beneficial[6].

Studies on modified bentonites have shown how humic acids influence the surface structure, promote porosity, and enhance adsorption capacity. These materials exhibit characteristic IR peaks around 3300–3400 cm^{-1} (O–H stretching) and near 1000 cm^{-1} (PO_4^{3-} vibrations), which are typical of organo-mineral composites.

Recent research has shown that the incorporation of humic acids into phosphorite-based materials significantly increases the number of adsorption sites and surface area. For instance, Zhang et al. (2024) demonstrated that carbon-based sorbents derived from biological waste exhibit high porosity and ion-exchange capacity. Their study used combined IR and XRD techniques to confirm the presence of active phosphorus forms[7].

Abenojar et al. (2023) effectively applied IR spectroscopy and electron microscopy to study the thermal and mechanical transformations in diatomite-based composites. These methods were particularly useful for analyzing the interaction between organic coatings and the mineral base, as well as for assessing the stability of functional groups and the occurrence of chemical reactions[8].

In conclusion, the proper characterization of organo-mineral materials derived from phosphorite sludge and humic acids—particularly for their potential use as fertilizers—requires the application of techniques such as IR spectroscopy and XRD. These methods provide critical insights into microstructure, bonding configurations, and phase transitions, which in turn help assess the practical applicability and efficiency of the materials in agricultural settings. This opens up new avenues for producing high-value, eco-friendly fertilizers from locally available raw materials[9-10].

II.MATERIALS AND METHODS

In this study, two primary instrumental analytical techniques—Infrared (IR) Spectroscopy and X-ray Diffraction (XRD)—were employed to investigate the compositional, structural, and functional characteristics of an organo-mineral composition based on phosphorite sludge and humic acid. These methods provide reliable data on the phase composition, chemical bonding, and interactions between the organic and mineral components of the material.

For sample preparation, phosphorite sludge was obtained in elongated granular form, dried under natural conditions, and mechanically ground to a particle size of less than 75 µm. Humic acid was used in its purified technical grade form. The organo-mineral composition was prepared by mixing the components in a 3:1 mass ratio to obtain a uniform, homogeneous blend. These mixtures served as the material basis for subsequent instrumental analyses.

FTIR analysis was conducted using a Nicolet 6700 Fourier Transform Infrared Spectrometer. The sample was mixed with KBr in a 1:100 mass ratio and pressed into pellets under 10 tons of pressure using a hydraulic press. The analysis was carried out in the range of 4000–400 cm^{-1} with a spectral resolution of 4 cm^{-1} and 64 scans per sample. These parameters ensured accurate and low-noise spectral data suitable for identifying characteristic absorption bands. The obtained spectra were baseline corrected. Distinct vibrational peaks corresponding to functional groups such as C–H, O–H, C=O, CO_3^{2-}, PO_4^{3-}, Fe–O, and Ca–O were identified and interpreted based on their specific wavenumber regions.

X-ray diffraction analysis was performed on a Rigaku D/MAX 2200 PC diffractometer using CuKα radiation ($\lambda = 1.54178$ Å) as the X-ray source. The scan was conducted over a 2θ range of 5°–70°, at a scanning speed of 4°/min with a step size of 0.02°. These conditions provided high-resolution data suitable for precise identification of crystalline mineral phases. The positions and intensities of the observed diffraction peaks were compared with standard reference patterns from the International Centre for Diffraction Data (ICDD) database.

Based on the XRD results, the phase composition of the material was determined, including the identification of phosphate phases, calcium and iron oxides, carbonates, and potential chelate compound formations. The sharpness, distribution, and angular positions of the peaks provided insights into the crystallinity of the structure and the degree of transformation during sample formation.

Overall, the combined use of FTIR and XRD in this research enabled a comprehensive characterization of the phosphorite sludge–humic acid-based organo-mineral composite. These complementary methods allowed for detailed analysis of both organic and mineral components, the nature of chemical bonding, and the structural reorganization induced by interaction. This methodological approach provides a robust foundation for evaluating the material's potential as an organo-mineral fertilizer in agricultural applications.

III.RESULTS

The presented XRD pattern (Figure 1) was obtained to investigate the crystalline structure and phase composition of the phosphorite sludge sample. The diagram shows the main diffraction peaks in the 2θ angular range, along with their corresponding d-spacing values. The high-intensity peaks observed on the diffractogram confirm the presence of phosphate minerals, especially apatite and its derivatives such as fluorapatite and carbonate-apatite.

The most intense peak appears around 2θ ≈ 31.8° (d = 3.03 Å), which corresponds to the principal diffraction line of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), indicating that crystalline apatite is the dominant phase in the sample. Additional peaks observed at approximately 2θ ≈ 25.9° (d = 3.43 Å), 32.2° (d = 2.84 Å), 34.2° (d = 2.62 Å), 39.9° (d = 2.29 Å), and 46.7° (d = 1.94 Å) are also associated with various crystal planes of apatite.

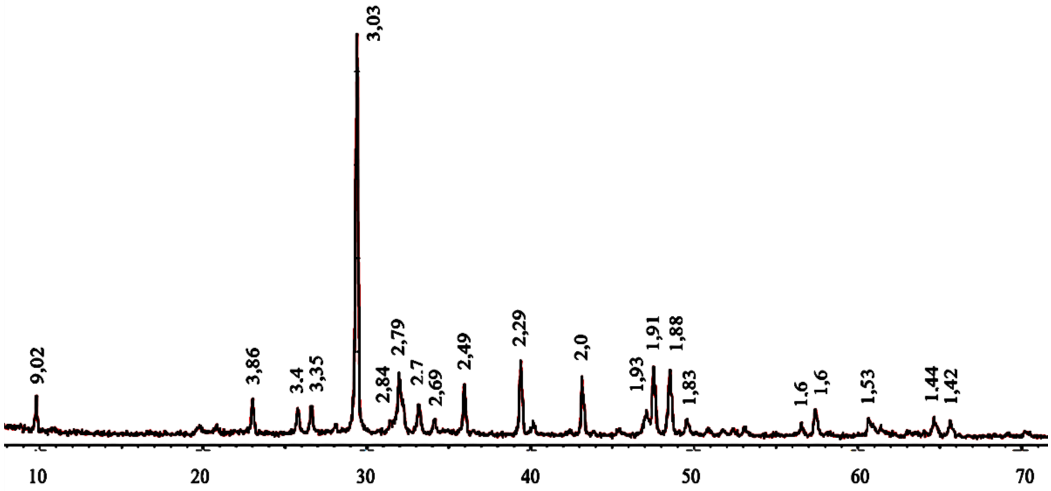

Figure 1. X-ray diffraction (XRD) pattern of the phosphorite sludge sample

Beyond phosphates, the presence of peaks at 2θ ≈ 26.7° (d = 3.34 Å) and 29.4° (d = 3.03 Å) suggests the existence of calcite ($CaCO_3$), indicating the presence of calcium-carbonate phases within the sludge. Peaks in the region of 2θ ≈ 50°–60° may be attributed to quartz (SiO_2) or dolomite ($CaMg(CO_3)_2$), indicating the presence of mixed mineral phases.

Moreover, the low intensity and broadness of some peaks imply the presence of amorphous phases in the phosphorite sludge, which may be related to its natural organic content. The presence of humic substances or bitumen can reduce the overall crystallinity of the material.

This (Figure 2) Fourier-transform infrared (FTIR) spectrum of the phosphorite sludge sample was recorded to identify the functional groups and both organic and mineral components of the material, within the wavenumber range of 4000–400 cm^{-1}.

In the high-frequency region (stretching vibrations), broad and weak absorption bands appear around 3690, 3629, and 3568 cm^{-1}, corresponding to the stretching vibrations of hydroxyl (–OH) groups typically present in phosphate minerals such as hydroxyapatite. Additionally, a broad absorption between 3400–3200 cm^{-1} is attributed to physically or chemically bound water molecules (adsorbed or crystallization water). The peaks at 2924 and 2854 cm^{-1} correspond to C–H stretching vibrations of aliphatic hydrocarbon chains, indicating the presence of organic matter such as humus, bitumen, or added biomass.

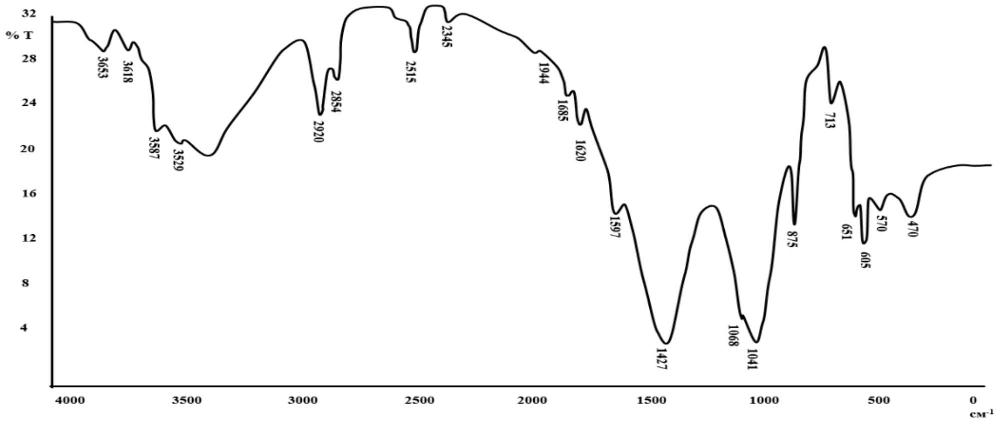

Figure 2. Infrared (FTIR) spectrum of the phosphorite sludge sample

Mid-frequency bands characteristic of mineral phases are observed at 1461, 1411, 1085, and 1041 cm⁻¹. Peaks at 1461 and 1411 cm⁻¹ are associated with the asymmetric stretching of carbonate (CO_3^{2-}) groups, which indicates the presence of calcite ($CaCO_3$) or carbonate-substituted apatite. The strong bands at 1085, 1041, and 985 cm⁻¹ are due to the asymmetric stretching vibrations of phosphate (PO_4^{3-}) groups, confirming the presence of hydroxyapatite and related phosphate salts.

The absorption band at 875 cm⁻¹ corresponds to the out-of-plane bending of carbonate anions, further suggesting the presence of carbonate minerals like calcite or dolomite. Low-frequency bands at 713 and 661 cm⁻¹ are also assigned to bending modes of PO_4^{3-} groups. Bands below 470 cm⁻¹ are associated with the lattice vibrations of phosphate or silicate groups.

In summary, the FTIR spectral data indicate the presence of phosphate (PO_4^{3-}), carbonate (CO_3^{2-}), and hydroxyl (–OH) groups within the phosphorite sludge. Furthermore, characteristic features of organic matter were also detected. These findings scientifically support the potential application of phosphorite sludge in the formulation of phosphate-based fertilizers.

This (Figure 3)X-ray diffractogram represents the phase composition of the sample prepared from phosphorite sludge and humic acid. The results reveal several distinct crystalline phases and structural transformations. The analysis indicates that the addition of humic acid to phosphorite sludge leads to a transformation of the primary phosphate compounds, accompanied by compositional and structural changes.

The most intense diffraction peaks are located within the 2θ range of 25°–35°, which correspond to phases such as $Ca_5(PO_4)_3OH$ (hydroxyapatite) or $Ca_5(PO_4)_3F$ (fluorapatite). Notably, the peaks located at 3.03 Å, 2.89 Å, 2.79 Å, 2.66 Å, and 2.57 Å are characteristic of phosphate (PO_4^{3-}) group vibrations, indicating the conversion of phosphorus into a crystalline phase and the formation of more bioavailable phosphate species under the activating influence of humic acid. This transformation can be attributed to the activation of phosphorus pentoxide (P_2O_5) within the mineral matrix.

1)

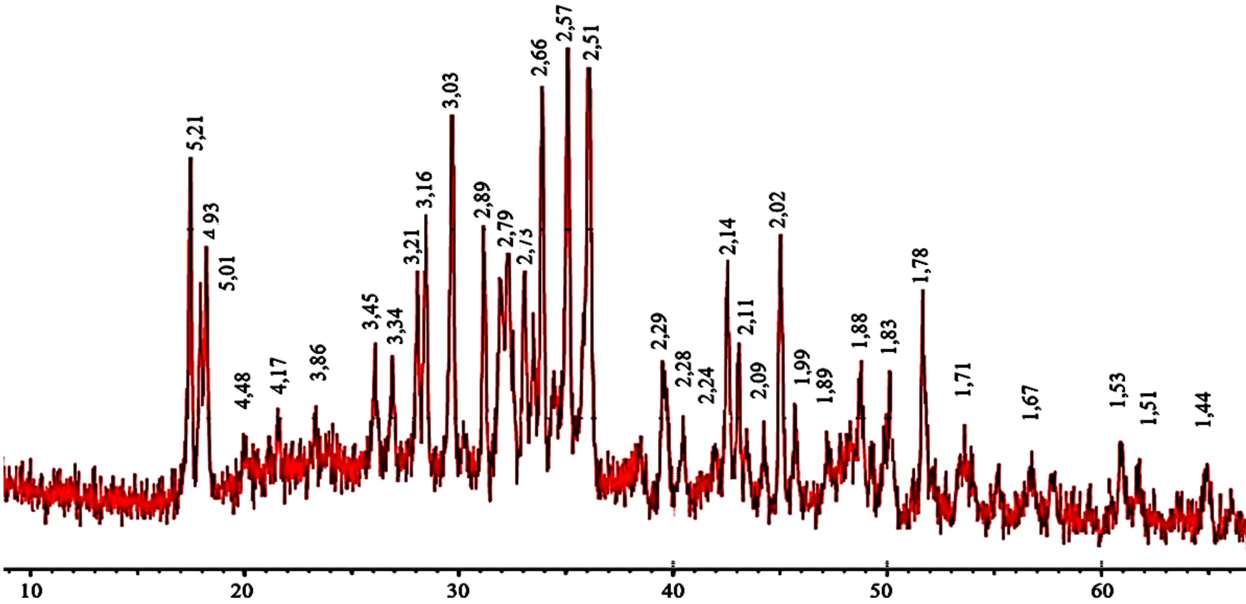

Figure 3. X-ray Diffraction (XRD) Pattern of the Sample Based on Phosphorite Sludge and Humic Acid

Interestingly, the appearance of high-interference peaks at 5.21 Å, 5.01 Å, and 4.93 Å suggests the formation of multi-component complexes under the influence of humic substances, likely representing organo–inorganic hybrid phases. These peaks may have developed during the decarbonation process, in which earlier-present carbonates such as $CaCO_3$ or $CaMg(CO_3)_2$ were decomposed. As a result, the characteristic carbonate peaks in the 3.8–4.0 Å region were reduced or disappeared entirely.

Additionally, the peaks observed in the $2\theta \approx 47°–50°$ range (2.02 Å, 1.99 Å, and 1.91 Å) may correspond to locally ordered structures of sulfate, nitrate, or calcium phosphate salts. These reflections indicate the formation of new crystalline phases through ion exchange and chelation reactions with humic acids. This behavior is supported by the known complexing ability of humic substances, which can chelate cations such as P, Ca, Fe, and Mg, enhancing the sample's adsorption activity.

The peaks at 2.29 Å, 2.22 Å, and 2.14 Å suggest the presence of hydrated phosphate or mixed calcium–magnesium salts localized in mesoporous or microstructural domains, acting as active adsorption centers. While the presence of these peaks confirms local crystallinity, the overall broad background in the XRD pattern suggests a significant proportion of amorphous content in the structure.

Furthermore, sharp peaks in the high-angle region (1.44–1.53 Å) may correspond to strongly crystalline phases such as calcium sulfate or the anorthite forms of calcium phosphate. These are indicative of re-crystallization processes involving activated calcium ions influenced by the humic acid environment.

In summary, the observed structural changes in the crystalline lattice of the sample based on phosphorite sludge and humic acid point to a transition of phosphorus into more reactive and bioavailable forms, the breakdown of carbonates, and the formation of new adsorption-active centers. Such materials can serve as highly effective organo-mineral fertilizers for agricultural use.

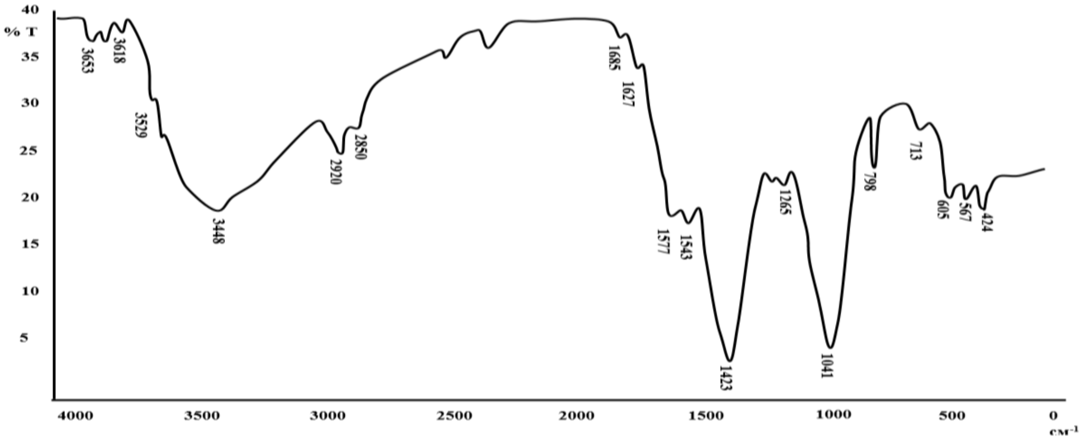

Figure 4. FTIR Spectrum of the Sample Based on Phosphorite Sludge and Humic Acid

This (Figure 4) infrared (FTIR) spectrum illustrates the main functional groups present in the sample prepared from phosphorite sludge and humic acid. It provides insight into the material's potential as an organo-mineral fertilizer, reflecting its composition and chemical transformations. The presence of numerous characteristic peaks indicates interactions between organic and mineral components, involving both covalent and ionic bonding.

In the 4000–3000 cm^{-1} region, absorption bands near 3435 cm^{-1} and 3366 cm^{-1} correspond to the stretching vibrations of O–H bonds. These peaks confirm the presence of hydroxyl groups from humic acids and adsorbed water molecules. Such hydrophilic groups play an important role in capturing ions in solution and supporting nutrient uptake. The bands at 2930 cm^{-1} and 2850 cm^{-1} are attributed to C–H stretching vibrations, indicating the presence of aliphatic chains from humic substances.

In the region of 1700–1500 cm^{-1}, the peaks at 1627 cm^{-1} and 1577 cm^{-1} correspond to the vibrational modes of carboxyl and carbonate groups. These bands relate to –COOH groups from humic acids and calcium carbonate ($CaCO_3$) content from phosphorite. Their strong intensity and clarity suggest the formation of chelates or ion-exchange complexes between the humic acids and mineral components.

The peaks at 1423 cm^{-1} and 1324 cm^{-1} represent C–O vibrations associated with carbonate or phenolic structures, reflecting the polyfunctional nature of humic acids and their ability to simultaneously interact with carbonate, phenolic, and ether groups. These functional groups enhance the capacity to adsorb and retain nutrients essential for plant growth.

The absorption bands between 1001–875 cm^{-1} are characteristic of PO_4^{3-} groups, indicating the preservation of phosphate structures within the phosphorite sludge. Prominent peaks at 1014 cm^{-1} and 945 cm^{-1} confirm the presence of phosphate compounds such as $Ca_5(PO_4)_3OH$ (hydroxyapatite) and $CaHPO_4$, which may form more bioavailable phosphorus species through interactions with humic acids.

In the low-frequency region, peaks at 713 cm^{-1}, 605 cm^{-1}, and 541 cm^{-1} are associated with Ca–O and Fe–O bonds, indicating the presence of calcium and iron oxides, hydroxides, or sulfates within the phosphorite sludge. These elements may be involved in structural reconfiguration and enhancement of ion-exchange properties due to humic acid influence.

Overall, the FTIR spectrum confirms that humic acid interacts with phosphorite sludge to form an organo-mineral material rich in reactive sites. The resulting compound exhibits high adsorption capacity and phosphorus bioavailability, making it a promising candidate for use as an organo-mineral fertilizer in agriculture. The identified functional groups and their bonding interactions enhance the material's stability, biological activity, and agronomic value. This type of material contributes to the conversion of phosphorite waste into valuable fertilizers.

IV.CONCLUSION

The conducted study demonstrates that organo-mineral materials derived from phosphorite sludge and humic acid hold significant potential as promising fertilizers for agricultural use. Structural and phase analysis methods—specifically X-ray diffraction (XRD) and Fourier-transform infrared (FTIR) spectroscopy—provided critical insights into the composition and functional group distribution of the composite material. The FTIR spectra revealed characteristic bands corresponding to –OH, –COOH, PO_4^{3-}, Ca–O, and Fe–O groups, indicating that humic acid reacts with phosphorite sludge through the formation of strong covalent and ionic bonds. This, in turn, enhances the number of active sites and promotes the formation of bioavailable nutrient forms easily assimilated by plants.

XRD analysis confirmed the processes of decarbonation and structural transformation of phosphate phases, facilitating the conversion of phosphorus into more soluble and plant-accessible forms. The interaction between humic substances and mineral phases led to the formation of stable organo-mineral complexes with increased porosity and functional diversity—key factors in improving nutrient retention and release in soil.

In summary, structural and phase characterization revealed that organo-mineral materials synthesized from phosphorite sludge and humic acid can serve as effective and environmentally safe alternatives to traditional mineral fertilizers. The stability, porosity, and abundance of active functional groups of these composites not only enhance plant nutrition efficiency but also open up possibilities for their application in wastewater treatment through biosorption. Thus, this integrated approach offers a valuable route for converting industrial phosphorite waste into high-value agricultural products with multifunctional environmental benefits.

REFERENCES

1. Visentsev, A. V., Bondareva, L. N., Gerasimova, E. P., & Orlova, A. A. (2018). Composite sorbents based on clay minerals and hydroxyapatite for the removal of heavy metal ions. *Izvestiya Vysshikh Uchebnykh Zavedenii. Khimiya i Khimicheskaya Tekhnologiya*, 61(6), 25–30.
2. Ivanets, A. I., Gerasimenko, A. A., Golikov, A. P., et al. (2017). Composite sorbent based on bentonite-like clay and hydroxyapatite for the removal of Cu(II) and Zn(II) ions from aqueous solutions. In *Proceedings of the 13th International Mine Water Association Congress* (pp. 1055–1061).
3. Vishnyakova, A. A. (1978). *Phosphate Fertilizers from Karatau, Gulyab, and Other Phosphorites*. Tashkent: Fan. (in Russian)
4. Bagreev, A., & Bandosz, T. J. (2001). On the importance of carbon surface chemistry in development of metal oxide–carbon composites for environmental applications. *Carbon*, 39(13), 1971–1979.
5. Alshameri, A., Yan, C., Ibrahim, A., Zhou, C., & Wang, H. (2018). Enhancement of heavy metals removal from aqueous solution by organo-bentonite modified with calcined magnesite. *Applied Clay Science*, 152, 323–332.
6. Zhang, Y., Wang, W., Wu, S., Guo, R., & Gao, C. (2024). Facile synthesis of porous magnetic carbon-based sorbent derived from low-cost biowaste for enhanced Pb(II) removal: Adsorption performance and mechanism. *Science of the Total Environment*, 920, Article 171011.
7. Abenojar, J., Sánchez, P. J., Encinas, N., Martínez, M. A., & Velasco, F. (2023). Surface treatment of diatomite to improve the performance of epoxy-based composites. *Journal of Composite Science*, 7(5), Article 310.
8. Kurnakov, N. S., & Petrov, A. A. (1975). *Fundamentals of Physicochemical Analysis*. Moscow: Khimiya. (in Russian)
9. Shibanova, O. Yu., & Noskova, E. V. (2008). *Spectroscopic Methods for Substance Analysis*. Novosibirsk: Novosibirsk State University. (in Russian)
10. Temirov, U. Sh., Sultonov, B. E., & Kholmatov, D. S. (2024). Utilization of phosphate waste and sewage sludge to obtain organo-mineral fertilizers. *Obogashchenie Rud*, (4), 39–43.