Ann. For. Res. 65(1): 845-853, 2022
DOI: 10.5281/zenodo.7262729

ANNALS OF FOREST RESEARCH
https://www.e-afr.org/

VARIABILITY OF SOME FUNCTIONAL GROUPS OF THE IR SPECTRA OF PHOSPHORITES AFTER INTERACTION WITH MICROFLORA AND ACID TREATMENT

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Abstract: The article discusses the current problems of enrichment of low-grade phosphorites by thermal method, as well as the production of mineral fertilizers using various acids. An alternative biotechnological method for obtaining organomineral fertilizers using neutrophilic, heterotrophic microorganisms of the activated sludge of a biochemical purification station for processing low-grade phosphorites and obtaining phosphorus-containing organomineral fertilizers is proposed. The acceleration of the processes of modification of phosphorus cemented in the minerals of granular phosphorites, resembling the natural cycle of phosphorus in nature, is noted. A comparative description of functional groups in the IR spectra after microbiological treatment and subsequent treatment with sulfuric and nitric acids showed the transition of valuable components of phosphorus compounds to a state assimilated by plants. The performed studies can serve as a basis for the disposal of low-grade phosphorites unused in production.
Keywords: active sludge, microflora, microorganisms, neutrophils, heterotrophs, functional groups, IR spectra, aerotanks.

Introduction. Uzbekistan has created its own mineral resource base for the production of phosphorus-containing fertilizers. Phosphorite manifestations are found in many regions of Uzbekistan (Fergana, Surkhandarya, Tashkent, Navoi, Central Kyzylkum, Bukhara-Khiva and Karakalpak) [1]. But the most promising, in terms of industrial development, was the Central Kyzylkum region [2].

Recently, man-made human impact has led to global pollution of the entire surface of the Earth. Therefore, the time has come for a coordinated interaction between man and the biosphere in the production of not only mineral fertilizers, but also other consumer products, taking into account environmental factors.

The new method of biotechnological processing of phosphorites using microorganisms that we have applied is based on the principle of modeling the evolutionary processes of the formation of mineral deposits and the ability of certain types of microorganisms, under certain conditions, to use mineral compounds as a source of nutrition. Many types of microorganisms that make up the microflora of activated sludge (AS) of a biological treatment plant, being in the waste liquid, are able to absorb not only pollutants into the cell, but also destruct some insoluble minerals of mineral deposits. They, acting on minerals with their intra- and extracellular organic metabolites, subject them to biochemical transformations [3-5].

Therefore, the types of microorganisms inhabiting activated sludge, in terms of numbers and species diversity, differ significantly from those that exist in the natural environment. Those microorganisms that began to dominate in number among the rest, due to natural selection associated with the composition and properties of the nutrient medium of the aerotank created by wastewater, have high adaptive properties due to the conditions of their selective selection. This biomass contains colonies of bacteria and microorganisms, which ensure the release of carbon, biogenic and other elements from wastewater [6].

The evolutionary origin of mineral deposits, to some extent, is subject, first of all, to the influence of not only external environmental factors, but also the close interaction of the living organic world with the inorganic. In each activated sludge, the active principle for the primary destruction of inorganic minerals is the release of microorganisms in the form of extracellular metabolites, enzymes, which, together with cationic elements released from the mineral, can form metal-organic complexes - chelates that can be well absorbed by plants. For activated sludge, regardless of the nature of industrial production or industry, the main decomposers of minerals are primarily heterotrophic bacteria, micromycete fungi and algae.

For this, the purpose of the research was a comparative IR spectroscopic study of the distinctive features of the emergence of new functional groups: a) after processing low-grade phosphorites with the microflora of activated sludge of a biochemical treatment plant, as well as; b) treatment of phosphorites with concentrated sulfuric and nitric acids.

The objectives of the research included modeling in laboratory conditions the natural evolutionary processes of the phosphorus cycle in nature, establishing the mechanisms of destruction of calcite ($CaCO_3$) and francolite ($Ca_5(PO_4,CO_3)_3(F,O)$) in the composition of phosphorites, as well as studying the processes of obtaining positive results after acid treatment [7].

Object and methods of research. The object of the study was the low-grade phosphorite ore of the Central Kyzyl Kum from the Jerooy-Sardara deposit with the following, complex chemical composition containing a high amount of carbonates (Table 1) [8]:

Table 1

Chemical composition of phosphorites of the Central Kyzylkum

№ s\n	Name of connections	element content, %	№ s\n	Name of connections	element content, %
1.	P_2O_5	8,0-12,0	8.	CO_2	8-15
2.	Al_2O_3	1,5-3,0	9.	Fluorine	1,8-3,2
3.	SiO_2	6,0-8,0	10.	SO_3	2,5- 3,5
4.	CaO	42-48,1	11.	U	0,003-0,008
5.	MgO	2,5-3,5	12.	REE amount	0,04-0,089
6.	Fe_2O_3	0,6-0,8	13.	H_2O	10,0
7.	R_2O	0.9-1.4	14.	Insoluble residue	8,0-8,2

To fulfill the set goal and task of scientific research, the following laboratory studies were carried out at the Navoi State Mining and Technology University:
- studied the chemical and mineralogical composition of phosphorites and activated sludge;
- studies were carried out on the leaching of various elements from low-grade phosphorites using aerobic species of neutrophilic, heterotrophic species of microorganisms of activated sludge from a biochemical treatment plant;
- assembled reactors imitating aerotanks of a biochemical treatment plant, in which, at a ratio of T:L = 1:4 (T-phosphorite, L-activated sludge), insoluble phosphorite minerals - calcite and francolite - were destructed;
- sulfuric (H_2SO_4) and nitric acids (HNO_3) were used, which are used in the production of mineral fertilizers for comparative analyses;
- a study of the distinctive IR spectroscopic features of functional groups in the composition of phosphorites before and after the experiment was carried out.

The microflora of activated sludge from the biochemical treatment plant in the form of a liquid phase (L) was mixed with low-grade phosphorites and their waste in the form of sludge (T) in the ratio L:T=4:1.

After bacterial leaching for 14 days, the qualitative composition of the solid phase samples was analyzed on a SHIMADZU instrument (laboratory of NSMI, Department of Chemical Technology) of the IRTracer-100 IR-Fourier spectrometer brand, using the method of preparing pressed tablets in KBr. The absorption bands of infrared light correspond to antisymmetric wavelengths in the range from 400 to 4000 cm^{-1}.

Analysis and discussion of the obtained results: Activated sludge is a complex substance that is a microflora involved in the wastewater treatment process and is an amphoteric colloidal system. Organic compounds that are part of activated sludge contain from 70 to 90% of organic substances in the composition of living organisms. They are represented by 12 main types of protozoa. Bacteria are the main activators of sludge. In 1м^3 they contain up to $2x10^{14}$ [13].

Analyzes of the chemical composition of activated sludge and samples of activated sludge with phosphorites were performed at the Research Institute of General and Inorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan (Table 2) according to the main methods of M.M. Zharsky and M.M. Vinnik, adopted in inorganic chemistry [9-10].

Table 2.

Chemical composition of activated sludge of biochemical treatment plant

Composition of activated sludge, %								
moisture	organic matter	nitrogen	P_2O_5	K_2O	CaO	MgO	ash	dry weight
95,38	2,99	0,12	0,14	0,01	0,17	0,02	1,41	4,67
In terms of dry matter, %								
10,05	28,54	11,44	13,35	0,95	16,21	1,90	13,44	44,26

Table 2 shows that the composition of AS is rich in the main macroelements - nitrogen, phosphorus, potassium, calcium and magnesium oxides, which are necessary for the growth and development of plants. Therefore, AS from a biochemical treatment plant for municipal waste, after some refinement, in itself can serve not only as a ready-made organic fertilizer, but also as a factor where AS microflora is able to actively influence, transform and destruct insoluble mineral compounds in the composition of phosphorites.

To detect the variability of various types of functional deviations in the composition of phosphorites and AS when deciphering the peaks of the IR spectra, we used the monograph by K. Nakamoto and others [11] and based on them a summary table of the detected functional groups was obtained. An IR spectroscopic study of various options for the interaction of activated sludge microflora with phosphorites, features of various functional mobile groups of nitrogen-, potassium-, phosphate- and calcium ions can help to get an idea of the chemical and structural composition of a new type of organomineral compound obtained. On fig. 1 shows the IR spectrum of activated sludge, where the concentration of humic compounds is distributed over the entire length of the spectrum and covers wavelengths from 500 to 4000 cm^{-1}. Protein fractions are distributed in the wavelength range covering the spectrum along the length from 2 to 300 cm^{-1}. Phosphorus compounds in the form of P-O, P=O, P=S, P-O-P, O-P-O bonds are in the wavelength range from 500 to 1000 cm^{-1}. Functional nitrogen compounds are distributed in the form of KNO_3 and are in the spectrum of 1000 cm^{-1}, and ammonium, amine and ammonia bonds cover the range of fluctuations from 2400 to 3500 cm^{-1}. Potassium compounds are expressed as KNO_3 and Potassium hydroxide bonds, the first is in the range of 1000, 1600 cm^{-1}, and Potassium hydroxide is located in the 3600 cm^{-1} band. The detected macroelements are distributed in a very wide range of variation and, apparently, are in the composition of aromatic compounds.

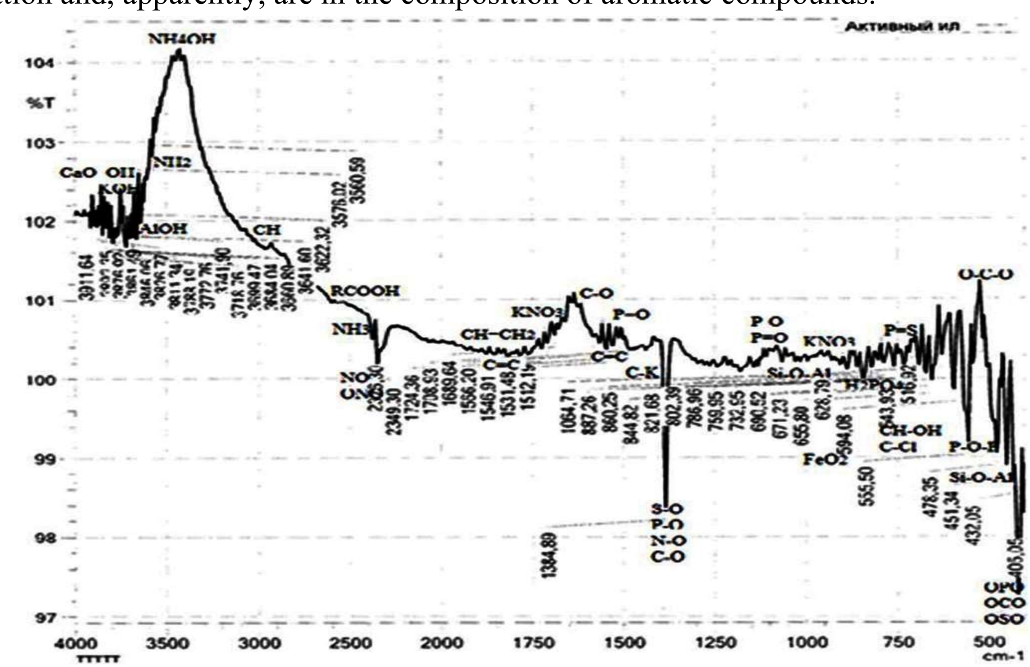

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Figure 1. Functional groups of the IR spectrum of activated sludge.

A more interesting picture and a wide range of wavelength variations in the distribution of functional groups were shown by the IR spectra of low-grade phosphorites (Fig. 2), where the spectra of francolite were clearly identified, covering wavelengths from 995 to 1600 cm^{-1}. Calcium compounds in the form of the mineral calcite were not only in the composition of francolite, but they were also distributed in the form of free calcite ($CaCO_3$) and CaO over wavelengths from 800 to 3800 cm^{-1}. The composition of phosphorite is actually very complex and includes aluminosilicate minerals - merwinite and forsterite (bands 460-466cm^{-1}), quartz (bands -1085-2090 cm^{-1}), phosphosiderite (bands 790-797cm^{-1}). The substitution of the PO_4^{3-} ion in the fluorapatite molecule by the CO_3^{2-} group can probably be judged by the shift of the maxima of the PO_4^{3-} vibration band to the high-frequency region due to the superposition of the carbonate absorption band in the composition of the phosphate mineral.

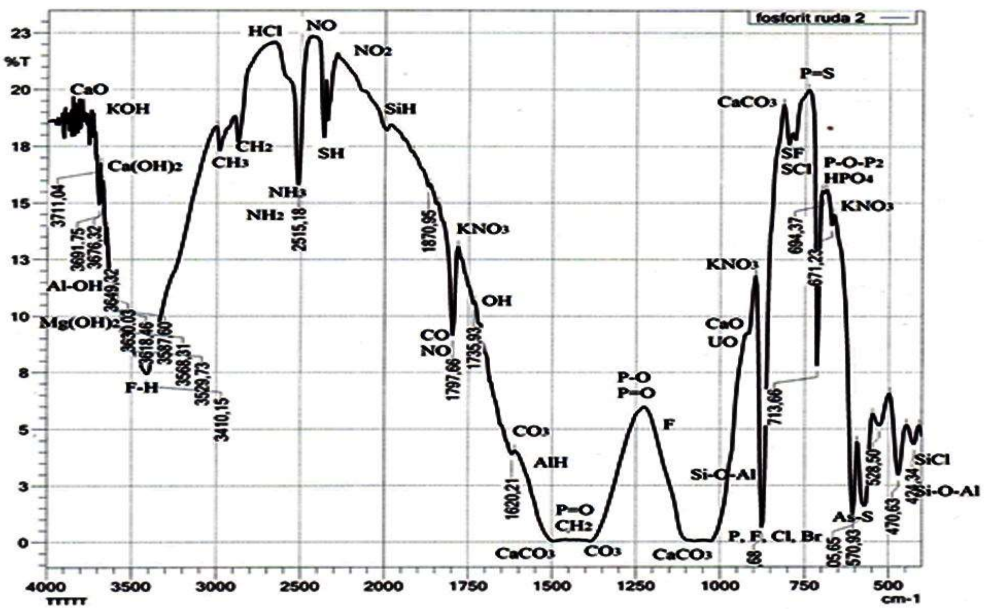

Figure 2. Functional groups of the IR spectrum of phosphorite ore.

Thus, on the IR spectra, we were able to determine the location of the main mineral of phosphorites - francolite in the composition of phosphorite ore, located within the wavelength range from 800 to 1800 cm^{-1}.

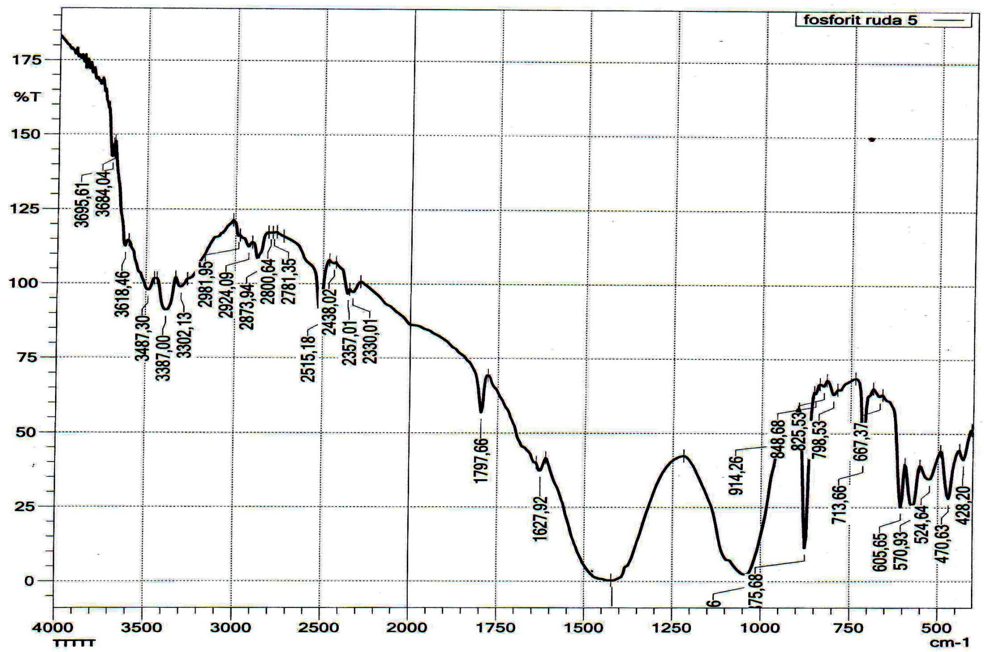

Figure 3. IR spectra of an option for activated sludge treatment of phosphorite ore.

After a comparative description of the IR spectra of activated sludge and phosphorites, phosphorite ore was added to the composition of activated sludge (AS) in the ratio T:L = 1:4, intensive aeration was turned on, which also mixed the organic matter of activated sludge with inorganic compounds of phosphorites, which led to a sharp change in the peaks of the IR spectra diagrams in Figure 3.

The main absorption bands of infrared radiation were already in the range from 3650 cm to 3950 cm^{-1}, which corresponds to such functional groups as $CaCO_3$, CaO, $Ca(OH)_2$, -O-H, COO-H-, X-H – that is, vibrations involving hydrogen atoms. It has been established that the absorption bands of IR rays of the samples under active exposure to air are practically the same, which indicates the important role of oxygen introduced into the aerotank. The microflora of AS, when interacting with phosphorite, caused the transition to an unstable state of many groups of elements. In a wide variety of compounds, calcite $CaCO_3$, was found, which turns into the following functional groups of elements - CaO, $Ca(OH)_2$, $CaSO_4$*H_2O.

Groups of alkaline earth elements have passed into weak bases - NaOH and potassium hydroxide. Chlorine ions turned into weak solutions of HCl, HOCl, $[ClO_3]^-$ and formed complexes in the form of $[CuCl_4]^-$. Phosphorus compounds underwent a significant change, turning into the following functional groups - $[PO_4]^{3-}$, P-OH, P=S, P-O, P=O, O-P-O, PO_4, HPO_4, H_2PO_4. The nitrogen element in the composition of AS has undergone minor changes and formed the following functional groups - KNO_3, NH_4NO_3, HNO_3, NH_3, RCOOH. The last compound - NH_3, RCOOH can be classified as an amino acid in proteins.

Upon microscopic examination of the samples, uneven, trapezoidal grains of francolite became rounded and became very small. Calcite under a microscope, having the form of marble blocks, was practically crushed and turned into small crumbs. The peaks of the IR spectrum, characteristic of calcite, corresponded to the functional groups $CaCO_3$, $CaSO_4*H_2O$. And such newly appeared functional groups as - PO_4, HPO_4, H_2PO_4, P=O, P-O, CH_2, CH_3C, $(CH_3)_2C$, $(CH_3)_3C$, $[SO_3]^{2-}$, HNO_3, KNO_3, are in the destroyed minerals in activated sludge compounds and belong to various types of cyclic aromatic compounds, most likely humic acids.

The conclusions made on the basis of the analysis of the characteristic lines of the IR spectrum confirm the data on the elemental composition of activated sludge containing impurities of low molecular weight substances and humic acids. Considering the high nitrogen content and the atomic ratios H/C, O/C, N/C, we can say that activated sludge is enriched with aliphatic and amine-containing functional groups.

Comparative characteristics of the absorption bands between phosphorite ores and AS showed that microorganisms actively interact not only with organic matter, but also with inorganic components of phosphorites, which is confirmed by IR spectrum diagrams.

When treated with sulfuric acid, the main reaction products of the stoichiometric amount of sulfuric acid and phosphorites were calcium sulfate and phosphoric acid. In practice, sulfuric acid processing of phosphorites with concentrated sulfuric acid is used at a stoichiometric ratio with phosphorite. As a result, superphosphate, double superphosphate are obtained as the final product, and extractive phosphoric acid (EPA) can be isolated. As a result, francolite breaks down to form phosphoric acid:

$Ca_5(PO_4)_3F + 5H_2SO_4 + 5нH_2O == 3H_3PO_4 + 5CaSO_4*нH_2O + HF$

Upon receipt of superphosphate, the following reaction occurs:

$2Ca_5(PO_4)_3F + 7H_2SO_4 + 3H_2O = 3Ca(H_2PO_4)_2*H_2O + 7CaSO_4 + 2HF$

In fact, an IR spectroscopic study showed that this does not actually happen, as some of the phosphorus, calcium, magnesium and fluorides remain in the sediment and are lost in the waste. In addition to this, during acid treatment, an exothermic reaction occurs, during which the solution boils with the release of abundant foam. Then the solution quickly thickens and turns into a dense pasty mass. Subsequently, when the solution is separated into solid and liquid parts, filtration is very slow and difficult. Despite the predominance of the sulfuric acid extraction method in the industrial production of phosphate fertilizers, the latter has a number of disadvantages, in particular, the formation of large amounts of waste in the form of phosphogypsum. In addition, the CaO/P_2O_5 ratio, which is excessive compared to phosphorite, requires a large amount of acid for decomposition and leads to the release of a larger amount of phosphogypsum [12].

The chemistry of the processes of nitric acid opening of phosphorites is quite complicated due to the multicomponent nature of the system. During the process, the main chemical reactions take place:

$Ca_5(PO_4)_3(F, OH) + 10HNO_3 = 5Ca(NO_3)_2 + 3H_3PO_4 + HF(H_2O)$

$(Ca,Mg)CO_3 + 2HNO_3 = (Ca,Mg)(NO_3)_2 + CO_2 + H_2O$

The sesquioxides and iron(II) oxide decompose to form nitrates:

$$R_2O_3 + 6HNO_3 = 2R(NO_3)_3 + 3H_2O \qquad \text{где } R – Fe, Al.$$

Phosphates of aluminum and iron, formed during the reaction, are poorly soluble in water and are poorly absorbed by plants. At the same time, aluminum oxide is a less harmful impurity. Iron oxide (II) decomposes with the release of nitrogen dioxide:

$FeO + 4HNO_3 = Fe(NO_3)_3 + NO_2 + 2H_2O$

In addition to iron (II) oxide, the sources of nitrogen oxides are organic impurities that reduce nitric acid, as well as technical nitric acid itself, containing a certain amount of nitrogen dioxide [12].

Conclusion. With the intensification of the processes of interaction of AS microflora with low-grade phosphorites and their waste in the form of sludge, a natural organic fusion of microflora and organic sediment of AS with phosphorites was noted. In parallel with this, the reverse process of the phosphorus cycle in nature was intensified, causing the process of the transition of an indigestible form of phosphorite into an assimilated one. The interaction of humic acids with silicates and aluminosilicates in phosphorites occurred due to the bonding of carboxyls of humic substances with OH groups of inorganic compounds. Nitrogen-containing groups of organic molecules can also take part in the formation of bonds between organic and inorganic substances. An analysis of the IR spectra of variants with activated sludge showed an active interaction of the AS microflora with phosphorite ore, where a shift of the bands in the region of high or low frequency spectra was noted. Francolite covering wavelengths from 800 to 1800 cm^{-1} after exposure to AS microorganism becomes less dense and decreases in size, and the band width narrows somewhat. This circumstance emphasizes the active influence of AS microorganisms on the composition of francolite, where francolite, which manifests itself in the form of microscopically uneven brown phosphorite grains, becomes finer, and phosphorus compounds and other elements pass into a soluble form. The new functional groups that appeared under the influence of microorganisms with oscillating spectra of molecules, in turn, have great activity, since there is a change in the valence of molecules that cannot exist in a stable state and therefore they combine with other functional groups, which leads to the formation of a new formation of minerals and chelate compounds.

Acid treatment of phosphorites has led to a rough distribution of valuable components in the solution and sediment, which leads to a low quality of the resulting mineral fertilizers.

Thus, the study of the IR spectra of activated sludge, phosphorite ore in various variations with activated sludge made it possible to accelerate the natural mechanisms of the phosphorus cycle in nature with the prospect of obtaining a qualitatively new organo-mineral fertilizer, as well as the selection of a special technological scheme for processing low-grade phosphorite ore. An analysis of the IR spectra also made it possible to establish the presence of granular francolite, which, under the influence of microflora, became looser due to the separation of calcite from its composition.

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