Fourier transformation of infrared spectroscopy and X-ray diffraction analyses of NPK mineral and biomineral fertilizers

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Abstract. In this study, Fourier Transform Infrared Spectrophotometry (FTIR), X-Ray Powder Diffraction (XRPD), comparatively employed to provide a quick, relatively inexpensive and efficient method for identifying and quantifying of NPK fertilizers of the AGRO series and their immobilized by the bacteria Bacillus Subtilis BS-26. A comprehensive spectroscopic study of NPK fertilizers of the AGRO series was reported first in the IRTracer-100 spectra (400-4000 cm-1) and the mineralogical composition of the these fertilizers was carried out by Powder X-Ray diffractometry Lab-X, XRD-6100 using corporation Shimadzu, Japan at room temperature. For analysis, the initial pure form of fertilizers AGRO series such as AGRO-01, AGRO-02, AGRO-03, AGRO-04 and their immobilized by Bacillus Subtilis BS-26 bacteria were selected. Results were shown as pictures and diffraction patterns. They contain information on the samples’ mineralogical composition and provide specific important structural and functional information.

1. Introduction

The fertilizer industry faces a continuing challenge to improve its products to increase the efficiency of their use, particularly of NPK fertilizers, and to minimize any possible adverse environmental impact. Furthermore, developed technology of NPK fertilizer should not be power-and time consuming. This is done either through improvement of fertilizers already in use, or through development of new specific fertilizer types [1]. Recently, numerous quantities of various fertilizers have been prepared and technology have been developed such as controlled-release and water-retention products based on abundant natural and biodegradable polymers (chitosan, cellulose and carbohydrates) with addition of poly (acrylic acid-co-acrylamide) [2, 3]. That type of fertilizers plays key role as water retention materials for the renewal of arid and desert environment. Because developed fertilizers have attracted great attention towards reduction of irrigation water consumption, and lower the death rate of plants.

Should note that liquid of NP and NPK fertilizers is one of promising products. The process of liquid NP-and NPK-fertilizers preparation based on monoammonium phosphate (MAP) slurry ranged pH = 4.5; 5.5 and 6.5 was studied. To reach balanced NP and NPK fertilizers urea, urea-ammonia
mixture, and potassium chloride were added. There were studied the composition and rheology the liquid balanced fertilizers [4].

Modern agriculture has to be more productive, sustainable and environmentally friendly. Today, microbial-based biofertilizers are considered to be among key agricultural components that improve crop productivity and contribute to sustainable agro-ecosystems. It is a component that aggregates a variety of microbial-based bio-products whose bioactivities are essential to stimulate and improve biological processes of the intricate plant–microbe–soil continuum. In the review of Bargaz et al. described about macronutrients such as nitrogen (N), phosphorus (P), potassium (K), and sulfur (S) supplied by mineral fertilizers are vital to crop production, agriculturally beneficial microorganisms may also contribute directly - biological N2 fixation, P solubilization, and phytohormone production or indirectly - antimicrobial compounds biosynthesis and elicitation of induced systemic resistance, to crop improvement and fertilizers efficiency. Microbial-based bioformulations that increase plant performance are greatly needed, and in particular bioformulations that exhibit complementary and synergistic effects with mineral fertilization. Such an integrated soil fertility management strategy has been demonstrated through several controlled and non-controlled experiments, but more efforts have to be made in order to thoroughly understand the multiple functions of beneficial microorganisms within the soil microbial community itself and in interaction with plants and mineral resources. In fact, the combined usage of microbial and mineral resources is an emerging research area that aims to design and develop efficient microbial formulations, which are highly compatible with mineral inputs, with positive impacts on both crops and environment [5].

Fourier Transform Infrared (FTIR) spectroscopy is a non-destructive and easy analytical technique that only requires small amounts of sample to provide information about the sample and functional groups of molecules based on the FTIR spectrum. The FT technique is the only method, which is rapid and can give the broadband absorption spectra of the sample simultaneously. Spectra arise from the vibrations of molecular bonds related to biochemical changes, and with the interactions between the organic components providing molecular fingerprints of the sample [6].

FTIR spectroscopy is an effective tool for chemical analysis of NPK fertilizers. This technique presents a rapid, inexpensive, and rather non-invasive method for obtaining chemical characteristics of fertilizer samples. It enables the identification of the main functional groups and chemical bonds, thereby providing information on the biochemical compounds present in the sample [7].

X-ray powder diffraction is one of the most potential characterization tools and a nondestructive technique for characterizing both organic and inorganic crystalline materials. The method previously used for measuring phase identification, quantitative analysis and to determine structure imperfections of samples from various disciplines such as geology, polymeric, environ-mental, pharmaceutical, and forensic sciences [8].

Recently the demands on quantity of fertilizers and even greater degree, on their quality have been characterized by steadily growing. Any improvement of their properties, particularly of their shipping and storage characteristics, would not be possible without the knowledge of their phase composition. The information on the phase composition of a freshly made fertilizer and the observation of its changes with time make it possible to understand and influence the mechanism of a number of processes taking place in fertilizers and affecting such important properties as the caking tendency and mechanical strength of their granules. The only method that enables this phase composition to be determined directly is X-Ray diffraction analysis [9].

Recently has been studied the X-Ray diffraction analysis to study the composition, crystallinity, physicochemical properties of mineral and biomineral fertilizers, such as «FAN-AGRO-03», «FAN-AGRO-04», «FAN-AGRO-07», «FAN-AGRO-09» and «FAN-AGRO-03/H2O», «FAN-AGRO-04/H2O», «FAN-AGRO-07/H2O», «FAN-AGRO-09/H2O» [10].

In this work, we report results FTIR spectroscopic and XRD characterization of solid NPK fertilizers of the AGRO series and its biomineral fertilizers immobilized by the bacteria Bacillus Subtilis BS-26.
2. Materials and methods

Different fertilizer samples were collected from the Limited Liability Company (LLC) of “FANDON”. Samples were transferred into polyethylene bags and tightly sealed, brought to the Laboratory of Physicochemical Methods of Research, Institute of Bioorganic Chemistry, Academy of Sciences of the Republic of Uzbekistan. The eight types of fertilizers like: AGRO-01 (I), AGRO-02 (II), AGRO-03 (III), AGRO-04 (IV) and immobilized by Bacillus Subtilis BS-26 bacteria AGRO-BIO-01 (V), AGRO-BIO-02 (VI), AGRO-BIO-03 (VII), AGRO-BIO-04 (VIII) were analyzed for different measurements.

The bacterial strain B. subtilis BS-26 isolated from the soil and that strain belong to the National Collection of Industrial Microorganism Cultures, Institute of Microbiology, Academy of Sciences of the Republic of Uzbekistan.

Fourier transform infrared spectroscopy analysis was performed on an IR Fourier spectrometer IRTracer-100 (Shimadzu, Japan), with a high signal-to-noise ratio of 60,000:1, a resolution of 0.25 cm$^{-1}$ and the ability to operate in a fast scan mode with recording up to 20 spectra per second. The spectra of the samples were recorded in a set with a single ATR attachment with a diamond / ZnSe prism MIRacle 10 in the scanning range of 4000 - 400 cm$^{-1}$.

The mineralogical composition of the I-VIII fertilizers was carried out by Powder X-Ray diffractometry Lab-X, XRD-6100 (Shimadzu Corp. Japan), using the standard Cu X-ray tube CuK$\alpha$ radiation ($\lambda$=1.5406 Å) Kβ Ni filter, scan range of 0°-2θ from 4° to 60° at 40 kV and 30 mA, 0.02 step size and 30 s time/step. XRD patterns were obtained two times: the first was initial AGRO fertilizers (I-IV) and the second after immobilization by strain of Bacillus Subtilis BS-26 (V-VIII).

3. Results and Discussions

The FTIR spectrum of samples I-VIII is recorded at room temperature. The wave number range is taken from 400 to 4000 cm$^{-1}$ as shown in Figure 1. The most intense bands of urea (CON$_2$H$_4$) are the C=O, N–H and C–N stretching frequencies appear at 1675.18 – 1643.35 cm$^{-1}$; 3430.40 – 3314.67 cm$^{-1}$ and 1097.50 – 1092.87 cm$^{-1}$.

In the I, IV and V substances observed another picture. Peaks of absorption bands C-N appears at 1002.98 cm$^{-1}$. The infrared absorption bands of monoammonium phosphate (NH$_4$H$_2$PO$_4$) at 1464.94 – 1433.11 cm$^{-1}$ can be assigned to the bending vibration mode of NH$_4^+$, peaks of absorption bands beside the 555.50 – 656.76 cm$^{-1}$ and 1147.65 – 1145.72 cm$^{-1}$ part of spectrum can be attributed to valence vibrations of tetrahedral form of PO$_4^{3-}$, the IR spectrums belong to functional groups of P=O; H$_2$PO$_4^-$; P-O-H; O=PO-H; O-H bendings vibration can be seen at 1283.63 – 1101.35 cm$^{-1}$; 889.18 – 786.96 cm$^{-1}$; 1097.50 – 1092.67 and 2841.32 – 2817.04 cm$^{-1}$; 1673.25 – 1643.35 cm$^{-1}$; 3324.31 – 3314.67 cm$^{-1}$ respectively.

The spectrum of magnesium sulphate heptahydrate (MgSO$_4$•7H$_2$O) was interpreted following the characteristic IR absorption bands for sulphate functional groups at 615.25 – 602.76 cm$^{-1}$; 786.96 – 716.56 cm$^{-1}$; 1104.25 – 1101.35 cm$^{-1}$. The bending of different water molecules of crystallization is observed at 3161.33 – 3073.57 cm$^{-1}$ and 1589.34 – 1588.38 cm$^{-1}$.

In the substances of V-VIII observed the spectral profile of KH$_2$PO$_4$ with three smooth band peaks at 1279 cm$^{-1}$, at 1077 cm$^{-1}$ (PO$_4$ vibrations) and at 877 cm$^{-1}$ (PO$_4$(H$_2$)) vibration) with increasing transmittance values from the highest to the smallest wavenumber regions. The location and the identification of characteristic bands of functional groups are done through the existing tables in the literature [11], [12], [13], [14], [15].
Figure 1. FTIR spectra of samples: A-I, B-II, C-III, D-IV, E-V, F-VI, G-VII, H-VIII.
Figure 2 shows the XRD pattern of samples I-VIII powder. The peaks observed at 22.254°, 24.616°, 29.322° corresponds to (110), (101), (111) crystal planes of CO(NH$_2$)$_2$; the peaks at 16.695°, 23.710°, 29.055°, 45.257° are corresponds to (101), (200), (112), (312) crystal planes of NH$_4$H$_2$PO$_4$; the peaks at 14.725°, 16.574°, 19.718°, 20.550° are corresponds to (020), (120), (201), (121) crystal planes of MgSO$_4$•7H$_2$O; the peaks at 28.636°, 40.526°, 50.133°, 58.693° are corresponds to (200), (220), (222), (400) crystal planes of KCl; the peaks at 23.975°, 29.682°, 30.728°, 45.662° are corresponds to (200), (211), (112), (312) crystal planes of KH$_2$PO$_4$. Experimental and calculated values are in good agreement with the literature data [16], [17], [18].

During immobilization, the substances react under the influence of moisture. Given these arguments, it was assumed that ammonium dihydrogen phosphate and potassium chloride interact
accordingly equation as:

\[ \text{NH}_4\text{H}_2\text{PO}_4 + \text{KCl} \rightarrow (\text{NH}_4)_x\text{K}_{1-x}\text{H}_2\text{PO}_4 + \text{K}_x\text{Cl}_x + (\text{NH}_4\text{Cl})_{1-x} \]

As a result, the peaks of potassium chloride and ammonium dihydrogen phosphate are greatly reduced and crystalline phases \((\text{NH}_4)_x\text{K}_{1-x}\text{H}_2\text{PO}_4\) and \(\text{KH}_2\text{PO}_4\) also appear and the other hands urea forms inclusion compounds with ammonium chloride \(\text{CO(NH}_2)_2\text{NH}_4\text{Cl} (1:1)\) are generated.

4. Conclusion

Thus, it was found that the presence of functional groups in contents of solid fertilizers, which have been identified by FT-IR spectral analysis. The selected fertilizers were the most used in agriculture, namely: \(\text{CON}_2\text{H}_4\), \((\text{NH}_4)_2\text{HPO}_4\), \(\text{MgSO}_4\cdot7\text{H}_2\text{O}\), \(\text{KCl}\) and \(\text{KH}_2\text{PO}_4\).

The results of powder X-Ray diffraction study showed that after the treatment of the initial mineral fertilizers with the \(B. \text{Subtilis BS-26}\) strain, an increase in the amorphous phase was observed due to a decrease in the crystalline phase. This indicates the appearance of new phases as a result of the reaction of the initial components and the formation of supramolecular complexes. As a result, the water-solubility of fertilizers in samples of V-VIII was improved.

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