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Phosphorus-humus fertilizers based on oxidized licorice meal and phosphate raw materials

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ABSTRACT

Humus-containing organic and organo-mineral fertilizers play a key role in increasing soil fertility due to their high water-holding capacity, improved water permeability, and ability to reduce phosphorus fixation by calcium and magnesium ions in calcareous soils and by sesquioxides in acidic soils. Organic matter from livestock waste, peat, and brown coal can enrich fertilizers with humus. However, plant residues such as aspen bark, agricultural husks, and licorice root meal are among the most effective additives to produce organic fertilizers. The present study evaluates the synthesis of phosphorus-humus fertilizers in grain form using indicator phosphate rocks discovered in the Kyzylkum deposit, Turkmenistan, and oxidized licorice paste, treated with hydrogen peroxide and acetic acid. The methodology lab experiment consisted of three steps. In the first step, the oxidation behavior of finely ground licorice meal (particle size < 0.1 mm) was investigated using an aqueous hydrogen peroxide solution and acetic acid at mass ratios relative to the organic fraction of the licorice meal in the range of H_2O_2: CH_3COOH = 100 : (10–20) : (0.1–1). In the second step, the phosphate rock was decomposed by 92% sulfuric acid, requiring 30-80% equivalent amounts for monocalcium phosphate. In the third step, the resulting products were mixed with the oxidized licorice paste at a ratio of 100:10:1. This paper evaluates the optimal conditions for processing the phosphorus-humus fertilizer, also producing flowcharts for processing, such as phosphate, provided by each resource. The efficiency of this new technology is presented. The results suggest that low rock phosphate and waste licorice root are environmentally friendly and can be recommended as an alternate tool to reduce the use of high-consumption chemical fertilizers or time consuming conventional composting process.

Keywords: licorice meal, hydrogen peroxide, phosphorite, extractive substances, sulfuric acid, oxidation.

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Introduction

Worldwide experience in sustainable agriculture development and agro-chemical research proves the efficacy of organic and organo-mineral fertilizer use for maintaining soil fertility and obtaining higher plant yields. Thus, for example, organo-mineral fertilizer application was proven to enhance the efficiency of nitrogen use, soil, and corn yield [1]. Also, the prolonged use of organic manure along with mineral fertilizer increased soil organic carbon, availability of nutrients, and crop yield under the pearl-millet/wheat rotation system [2]. Therefore, the production and usage of such fertilizers from organic materials, phosphate materials, and agricultural ores, providing all essential nutrients for plant development, play an important role in improving agricultural productivity and sustainability.

In worldwide agricultural practices, soil fertility is assessed on the basis of three large categories of indicators: agrophysical, agrochemical, and biological. These components are intricately interlinked and contribute significantly to the ability of the soil to support the growth of plants in the surrounding environment. Agrophysical indicators are used to describe the physical state of the soil and consist of structure, particle size distribution, mineralogical constitution, porosity, air and water-holding capacity, and water permeability. These properties are generally much slower to change and can only be restored to their former state after a significant amount of time and difficult efforts when degraded [3]. The agrochemical component is used to describe the quantity and availability of vital nutrients like nitrogen, phosphorus, potassium, and other macronutrients and micronutrients. This property plays a pivotal role in defining the availability of nutrients for plants and directly affects the productivity of crops and their growth rate [4]. Biological components can be associated with the quantity, quality, and type of soil organic matter and microbial activity, along with the general phytosanitary status of the soil. However, in a large number of cases, the general standard of soil fertility can be attributed to the quality and quantity of the existing organic matter. Organic matter plays a highly significant role in defining the distinct characteristics of the soil, acting as the principal connecting link that defines the general state of soil fertility. Moreover, acting as a reservoir of carbon, nitrogen, phosphorus, potassium, and other nutrients, the role of soil organic matter can help ensure optimal fertility for plant development and can counterbalance the effects of toxic substances present in the surrounding soil and environment [[5], [6]].

Humification and mineralization of residue C in the soil by the microflora result in nutrient release. Data indicate that residue addition augments the concentration of C by 10-12% and that of N by 7-9% compared to fertilizer addition alone [[7], [8]]. Long-term studies indicate that when residue addition is coupled with the addition of mineral nutrients, about 5.5 t of C/ha carbon sequestration is possible in five years [[7], [8], [9]]. Moreover, residue addition to soils and subsequent microbial decomposition have been found to enhance carbon and nutrient cycling [[9], [10]]. It has been found that a meta-analysis of residue addition is effective in augmenting soil organic carbon concentration [[7], [11]]. Thus, organic matter addition to soils through residue addition is essential to maintain soil fertility and nutrient cycles [11].

According to [11], organomineral fertilizers promoted considerable increases in yield. The greatest values in terms of grain, straw, and sheaf weights were recorded with dung-lignin mixture at 60 t/ha, reaching 20.04, 23.60, and 43.89 g/vessel, respectively; this is a significant increase by 65-79% compared with the control. More or less similar yields (44-46 g/vessel) were recorded with semi-rotted manure at 60-80 t/ha and with dung-lignin mixture at 40 t/ha. At higher doses (80 t/ha), dung-lignin mixture and lignin-sludge mixture at 40 t/ha slightly lowered the oat grain yield, while straw and sheaf weight increased by 28-62%; thus, there is a tendency towards vegetative development. A limitation of this method is that the large volumes of fertilizer produced lead to substantial transportation costs.

The use of humic substances (HS) together with mineral fertilizers improves soil agrochemical properties and helps maintain long-term fertility. HS interacts with mineral particles to form stable organomineral complexes that effectively absorb moisture and dissolved nutrients. By binding soil particles, HS promotes the development of a water-resistant, loose, granular structure, which enhances both water infiltration and nutrient retention. As a result, nutrients remain available to plants rather than becoming fixed by soil minerals or lost through leaching [[12], [13]].

Paper [14] presents a method for producing phosphorus organomineral fertilizers with high resistance to nutrient leaching. Aspen bark is impregnated with KH_2PO_4 and converted into $Ca(H_2PO_4)_2$, resulting in a water-resistant product that can also be enriched with microelements. The improved resistance ensures a prolonged fertilizer

effect, and pot experiments confirmed its positive influence on plant growth. The preparation process has multiple stages, and generating effluent is not a term of an environmentally friendly approach.

In [15], phosphorus biocomposite fertilizers were produced by impregnating porous birch bast and bark with aqueous K_2HPO_4. The most effective conditions for reducing phosphate leaching were heating at 100 °C for 2 h, drying at 200 °C, and treating with 0.1 N HNO_3. The resulting materials, containing 3.5–4.0 wt.% P, released only ~35% of their phosphorus over 72 h, demonstrating prolonged nutrient release. Phosphorus loadings above 4 wt.% decreased water resistance. Overall, these birch-based biocomposites showed much higher resistance to leaching than standard granular fertilizers. Low concentration and time-consuming processing restrict the product's application on a wider scale.

Phosphorus has long been a key focus in agricultural chemistry because most soils contain little of it and its low mobility makes it poorly available to plants. At the same time, global reserves of phosphate raw materials are limited, and many are unsuitable for producing water-soluble fertilizers. Ensuring future food security requires more efficient phosphorus use and better understanding of its cycling in soil–plant systems, including the interactions between soil physics, chemistry, biology, and plant traits [[16], [17]].

Phosphate fertilizers are derived from natural phosphate ores—primarily phosphorites (≈85%), while apatite accounts for only about 6% of the estimated 75.1 billion tonnes of global proven reserves. In both ore types, the principal phosphorus-bearing mineral is calcium fluorapatite ($Ca_5(PO_4)_3F$), occurring mainly as fluorapatite and hydroxyapatite. The physical and chemical characteristics of phosphate ores vary depending on their mineral composition and impurity levels. One of the world's richest and most industrially significant apatite–nepheline deposits is located on the Kola Peninsula [[18], [19]].

Ten countries, such as Morocco, the United States, China, Russia, Mexico, Kazakhstan, Peru, South Africa, Western Sahara, and Tunisia, hold around 61,015.4 million tonnes of P_2O_5, or 87% of global phosphate reserves. Significant additional deposits have also been identified on the seabed and continental shelves [20].

The Kyzylkum phosphorite basin covers an estimated 65,000 km². Assuming that only 5% of this area contains industrially significant phosphorite beds, and using an average ore layer thickness of 2.5 m, the predicted geological reserves would amount to approximately 16.25 billion tonnes of phosphorite, or about 1.95 billion tonnes of P_2O_5 (based on an average P_2O_5 content of 12%) [68]. Phosphorite deposits occur in several regions of Uzbekistan, with the Central Kyzylkum area considered the most promising for industrial development. Four deposits have been identified: Jeroy-Sardara, Jetymtau, Tashkurin, and Karakatin. The best-studied is the Jeroy-Sardara deposit, which includes the Jeroy South, Kurukkuduk, and Tashkura sites. Total reserves are estimated at 384.4 million tonnes of ore, containing about 73.9 million tonnes of P_2O_5 [[21], [22]].

The most widely used phosphorus fertilizer globally is simple superphosphate (SSP), which consists primarily of water-soluble calcium dihydrogen phosphate, $Ca(H_2PO_4)_2$. It is produced by treating phosphate rock with sulfuric acid.

$$2Ca_5(PO_4)_3F_{(s)} + 7H_2SO_{4(l)} \rightarrow 3Ca(H_2PO_4)_{2(aq)} + 7CaSO_{4(s)} + 2HF_{(g)} \quad 1$$

However, after application SSP to neutral or calcareous soils, the readily soluble $Ca(H_2PO_4)_2$ is rapidly transformed into less soluble forms such as $CaHPO_4$ and $Ca_3(PO_4)_2$, which gradually supply phosphorus to plants as follows:

$$Ca(H_2PO_4)_{2(aq)}+Ca(HCO_3)_{2(aq)} \rightarrow 2CaHPO_4{\cdot}2H_2O_{(s)}+2CO_{2(g)} \quad 2$$

$$Ca(H_2PO_4)_{2(aq)}+2Ca(HCO_3)_{2(aq)} \rightarrow Ca_3(PO_4)_{2(s)} +4H_2O_{(l)} + 4CO_{2(g)} \quad 3$$

In that case, poorly soluble minerals such as hydroxyapatite or fluorapatite may form in the soil, making phosphorus unavailable for plant uptake [23].

In acidic soils (pH < 5.5), Al^{3+} is released from aluminosilicate minerals (e.g., clay minerals like kaolinite, gibbsite). Ferric iron (Fe^{3+}) released from geotite is the dominant form in well-drained acidic soils. Ferrous iron (Fe^{2+}) occurs in reducing or waterlogged conditions (wüstite, olivine, pyroxene, and troilite) and is more soluble [[24], [25]].

Therefore, in acidic soils rich in sesquioxides such as Al^{3+} and Fe^{2+}/Fe^{3+}, poorly soluble and difficult-to-utilize phosphorus compounds can form, reducing phosphorus availability to plants.

A simplified overall reaction:

$$Ca(H_2PO_4)_{2(aq)} + Al^{3+} \rightarrow 2H^+ + Ca^{2+} + AlPO_4 \downarrow \quad 4$$

$$Ca(H_2PO_4)_{2(aq)} + Fe^{2+} \rightarrow 2H^+ + Ca^{2+} + FeHPO_4 \downarrow \quad 5$$

$Ca(H_2PO_4)_{2(aq)} + Fe^{3+} \rightarrow 2H^+ + Ca^{2+} + FePO_4 \downarrow$ 6

Consequently, the application of phosphate rarely exceeds ~ 10–25 % efficiency, leading to the consumption of water-soluble phosphate fertilizers at rates significantly higher than the actual phosphorus demand [[26], [27]].

The significance and mode of action of organomineral fertilizers in agricultural production have been extensively discussed [[28], [29], [30], [31]]. Humic substances present in these fertilizers enhance the uptake of essential nutrients by plants. They prevent the retrogradation of readily assimilable phosphates, provide microelements and physiologically active compounds, improve soil structure, create favorable conditions for beneficial microorganisms, and ultimately stimulate plant growth and development. Organic and/or organomineral fertilizer raw materials may comprise manure, peat, lignin, sapropel, brown coal, and/or various plant organic materials. Composted agricultural by-products, including olive waste sludge compost, humic-rich organic materials, and/or other stabilized organic by-product materials, are also used extensively, besides being productive additives in the formulation of organomineral fertilizers [[28], [29], [30], [31]].

Naked licorice meal is a potential raw material for the production of humic fertilizers due to its high concentration of biologically active compounds. Licorice refers to a Glycyrrhiza species that is an herbaceous perennial and a legume family member. The licorice leaf is recognized for making medicinal preparations and decompositions, and the licorice hay, which has high protein nutrients, is used as animal feed [[32], [33]]. However, the root is considered the most pharmacologically significant part of the plant. Licorice root contains organic acids (malic, citric, and succinic), β-carotene, a broad spectrum of vitamins, and essential macro- and microelements including potassium, calcium, iron, phosphorus, and magnesium. The principal biologically active constituents are triterpenoid compounds, notably glycyrrhizic acid, along with a diverse group of flavonoids, which may constitute up to 25% of the root's chemical composition.

In Uzbekistan, more than thirty enterprises of various ownership types are involved in the procurement and processing of licorice root, primarily in the Khorezm and Bukhara regions and the Republic of Karakalpakstan. Licorice naturally grows in the Amu Darya and Syr Darya river deltas, where it thrives in tugai forest ecosystems, along irrigation networks, and on saline soils and fallow lands [34].

Turkmenistan is also a significant regional producer. In 2021, the country produced 680 tons of dry licorice extract; the Buýan agro-industrial complex alone generated 680 tons of dry and 610 tons of thick extract from 2,960 tons of purified licorice root. According to 'Turkmenistan: Golden Age,' the enterprise exceeded its production plan by 118.7%. Buýan is located in Turkmenabat and is involved in making licorice-based teas, extracts, balms, and capsules. It has been processing 17,500 tons of licorice root annually as of 2020 and 19,000 tons in 2022. These figures show enhanced processing capacities and their significance for the economy.

It is worth mentioning that after industrial processing of licorice root, a significant amount of licorice meal is obtained, namely, over 80% of raw material, with a yearly output exceeding 100,000 tons in Karakalpakstan alone, which is actually treated as industrial waste. Also, during the process, a liquid ammonium sulphate solution with a concentration of (0.5-1%) of 400,000 tons is obtained, with a significant amount of physiologically active compounds [[35], [36], [37], [38]].

The above-mentioned methods for producing organic and organo-mineral humus and/or humic-containing fertilizers based on composting are time-consuming and limited in their applicability to large-scale agricultural production. Moreover, the use of commercial fertilizers such as mono- and diammonium phosphate and triple superphosphate increases the final product cost. In contrast, the use of an aqueous hydrogen peroxide solution in the presence of acetic acid to accelerate the humification of licorice meal waste, combined with low sulfuric acid consumption for processing low-grade phosphate rock, has both academic and practical significance for applied chemistry and agrochemistry.

It has been found that the available literature provides no effective means to date to utilize the insoluble part of the licorice meal to produce valuable compounds like Humic Acids, Fulvic Acids, or Humic-Like Substances, the role of which is very important in increasing the fertility of the soil. It is important to note that no other similar work has been carried out on the licorice-root meal, the largest solid waste generated in the pharmaceutical industries, for the extraction of glycyrrhizic acid or other biologically active compounds.

Within this framework, the purpose of this study is to find and introduce a new method involving the oxidation of licorice meal by hydrogen peroxide in acetic acid solution and to make use of the resultant

oxidation substance in conjunction with the by-product derived from the decomposition of phosphate raw material with sulfuric acid for phosphorus-humus fertilizer production.

Experimental part

Licorice root meal served as the primary raw material for the study. The material was air-dried and subsequently ground to a particle size of 0.25 mm. Following drying and grinding, a composite representative sample exceeding 10 kg was prepared for analytical characterization and experimental work. Subsamples were collected to determine moisture content, ash content, and the amounts of water-soluble and alkali-soluble extractives.

The extractable organic fraction (EOF) of the initial and oxidized meal was determined using a procedure analogous to the standard method for isolating humic substances. Weighed sample of the meal was placed in a 250-mL flask A. 100 mL of a 1% alkaline sodium hydroxide solution is added, and the mixture is heated for 2 hours in a boiling water bath. After cooling, the contents of Flask A are centrifuged for 15 minutes at 210 $s^{-1,}$ and the supernatant is decanted. The residue was washed twice with 100 mL NaOH; all alkaline extracts were combined and filtered into a 500-mL volumetric flask B and made up to volume.

A 100-mL aliquot of this extract was acidified with 60 mL of HCl to precipitate high-molecular-weight organic acids. The precipitate was centrifuged, washed with water to the onset of peptization, and treated with an additional 5 mL of HCl to ensure complete precipitation. The precipitate was collected on a pre-dried ashless filter and dried to constant mass at 90 ± 5°C. The filter was then transferred to a crucible, ignited at 600 ± 25°C to constant mass, and weighed to determine both organic and ash fractions.

The mass fraction of soluble organic acids (SOA), recalculated to a dry ash-free basis, was calculated as:

$$\mathrm{SOA} = \frac{100 \cdot V(m_1 - m_2)}{V_1 \cdot m} \qquad 7$$

where m_1 and m_2 are the masses of the dried and ashed precipitate of SOA, respectively, g; V is the total extract volume, mL; V_1 is the volume of an aliquot of the alkaline solution taken for SOA precipitation, mL; m is the mass of the meal sample on a dry ash-free basis, g, calculated using the formula:

$$m = m_3 \cdot \frac{100-(W+A)}{100} \qquad 8$$

where m_3 is the mass of the meal sample, g, W, and A are the moisture and ash contents of the meal.

The organic portion (substance) (OS) of both liquid and solid phases represents the oxidized meal. Its yield was calculated from the organic content of the initial raw meal [[39], [40]].

The total content of phenolic and carboxyl functional groups in high-molecular-weight organic acids isolated from oxidized meal (0–0.25 mm fraction) was determined by alkalimetric titration. A 0.5 g sample was weighed with an accuracy of ±0.0002 g and treated with 50 mL of 0.1 N NaOH. The suspension was kept for 24 h with intermittent shaking, after which the solid phase was separated using paper filtration. An aliquot of the filtrate was transferred to a conical titration flask and titrated with 0.1 N HCl in the presence of phenolphthalein until the disappearance of the crimson color. A blank test (without oxidized meal) was performed under identical conditions.

The total acidity (phenolic + carboxyl groups) in mg-eq/g was calculated using:

$$N_{\mathrm{OH+COOH}} = \frac{(V-V_1)V_3 N_{\mathrm{HCl}}}{G\,V_2} \qquad 9$$

where: V is volume of HCl used for the blank, mL; V_1 is volume of HCl used for the sample of SOA, mL; V_2 is aliquot volume, mL; V_3 is volume of 0.1 N NaOH added to the sample, mL; NHCl is normality of HCl; G is sample mass of SOA, g.

Determination of carboxyl groups was performed analogously. A 0.5 g sample was treated with 0.1 N $NaHCO_3$, kept for 24 h, filtered, and an aliquot was titrated with 0.1 N HCl using methyl orange (yellow → crimson). Carboxyl group content was calculated using the formula above. The concentration of phenolic hydroxyl groups was determined as the difference between total acidity and carboxyl group content.

For the determination of carbonyl groups, a 0.5 g sample was treated with 50 mL of 0.1 N hydroxylamine hydrochloride, mixed, and left for 24 h. After filtration, an aliquot was titrated with 0.1 N NaOH in the presence of phenolphthalein until a stable crimson color appeared. Carbonyl group content was calculated as:

$$N_{\mathrm{C=O}} = \frac{(V-V_1)V_3 N_{\mathrm{NaOH}}}{G\,V_2} \qquad 10$$

where: V is NaOH volume for blank, mL; V_1 is VNaOH volume for used for titration of the solution with SOA, mL; V_2 is aliquot volume, mL; V_3 is volume of 0.1 N hydroxylamine hydrochloride added to the test sample, mL; N_{NaOH} is normality of NaOH; G is sample mass, g.

Phosphorite raw materials from Uzbekistan (Kyzylkum) and Turkmenistan (Durnals) were used in this study. The first sample was phosphate rock from the Kyzylkum deposit (Uzbekistan), characterized by the following chemical composition (%, by mass): P_2O_5 – 17.54; citric-acid-soluble P_2O_5 – 3.15; Trilon-B-soluble P_2O_5 – 3.76; CaO – 47.75; MgO – 1.79; Al_2O_3 – 0.90; Fe_2O_3 – 0.73; F – 1.70; CO_2 – 16.50; SO_3 – 4.06.

The proportion of plant-available phosphorus relative to total P_2O_5 amounted to 17.96% (citric acid) and 21.44% (Trilon-B).

The second raw material was phosphate rock from the Durnals deposit (Turkmenistan), with the following composition (%, by mass): P_2O_5 – 13.73; citric-acid-soluble P_2O_5 – 6.18; Trilon-B-soluble P_2O_5 – 2.96; CaO – 28.21; MgO – 1.10; Al_2O_3 – 1.10; Fe_2O_3 – 9.01; F – 1.08; CO_2 – 1.70; SO_3 – 21.55. Plant-available P_2O_5 relative to total P_2O_5 was 45.04% (citric acid) and 21.58% (Trilon-B or EDTA).

At the initial stage of the study, the oxidation behavior of finely ground licorice meal (particle size <0.1 mm) was investigated using an aqueous hydrogen peroxide solution in the presence of acetic acid. The reagents were applied in the following mass ratios relative to the organic fraction of the licorice meal:

$$H_2O_2: CH_3COOH = 100: (10–20): (0.1–1).$$

The experiments were performed in a cylindrical glass reactor with a thermostatic jacket and equipped with mechanical stirring. The oxidizing solution was first fed into the reactor, the set temperature was reached, and the stirrer was switched on. A weighed amount of the crushed licorice meal was then introduced to start the oxidation process.

After the reaction was complete, the mixture was dried to an air-dry condition. The obtained material was tested for ash content, moisture, organic matter, and extractable substances yield by 1% solution of sodium hydroxide. All analytical procedures were carried out by the methodologies given in references [[39], [40]].

The subsequent stage of the research was devoted to the preparation of phosphorus-humus fertilizers by decomposing phosphate rock of Uzbekistan and Turkmenistan with sulfuric acid. To activate the phosphate raw material, 92% sulfuric acid was used as the decomposing agent, ensuring effective dissolution of the reactive mineral phases and formation of the target phosphate–sulfate mixture suitable for subsequent incorporation with the oxidized licorice meal.

The first stage in producing phosphorus–humus fertilizers consisted of decomposing the phosphate raw material with sulfuric acid to convert the insoluble form of P_2O_5 into plant-available forms. The amount of sulfuric acid was varied and set to 10, 20, 30, 40, and 80% of the stoichiometric requirement for the formation of monocalcium phosphate, according to the following reaction:

$$CaO_{\text{in phosphorite}} + 2H_2SO_{4(aq)} \rightarrow Ca(H_2PO_4)_2 \cdot H_2O_{(s)} \quad 11$$

At a sulfuric acid dosage corresponding to 70% of the stoichiometric requirement, 50.58 g of 92% H_2SO_4 was needed to process 100 g of phosphate rock from the Uzbekistan deposit. In contrast, at 40% of the stoichiometric requirement, 5.84 g of 92% H_2SO_4 was sufficient to treat 100 g of phosphate rock from the Turkmenistan deposit.

The phosphate rock was decomposed with sulfuric acid for 60 min. Upon completion of decomposition, the oxidized licorice meal was introduced into the reaction mixture at a weight ratio of phosphorite: meal (organic portion) = 1: (0.20–1.00). The mixture was then stirred for 30 min and subsequently neutralized with 25% aqueous ammonia to a pH of 4.0–4.5. Drying was performed at 80 °C, and granulation was carried out by the pelleting method during the ammoniation and drying stages.

The chemical composition and mechanical strength of the resulting fertilizer granules were determined. The compressive strength of 2–3 mm granules was measured using an IPG-1M granule strength meter, yielding average values of 2.3–2.7 MPa.

All forms of P_2O_5 were quantified gravimetrically by precipitating phosphate ions with a magnesia mixture as magnesium ammonium phosphate, followed by calcination of the precipitate at 1000–1050 °C, in accordance with GOST 20851.2-75. Nitrogen was determined in accordance with GOST 26715-85. SO_3 was measured by precipitation as barium sulfate, and CaO was determined by titration with 0.05 N Trilon B using flurexon as the indicator.

X-ray diffraction (XRD) analysis was performed using a Shimadzu XRD-6100 diffractometer equipped with a CuKα radiation source (λ = 1.5406 Å), operated at 40 kV and 30 mA. Diffraction patterns were recorded in the 2θ range of 5–70° with a scan speed of 2°/min. Phase identification was conducted using standard domestic reference catalogs and the ASTM Powder Diffraction File (PDF) database [[41], [42], [43]].

Elemental analysis of the licorice meal ash was performed using an Agilent 7900 ICP-MS (Agilent Technologies, USA). Samples were introduced through a micro-mist nebulizer and quartz spray chamber under standard plasma conditions (RF power 1550 W). Helium collision mode (He-CRC) was used to suppress polyatomic interferences for elements such as Fe, Ca, Mg, and Ti. The instrument provides a full mass range (m/z 7–238), allowing accurate determination of all measured elements (Li, Be, B, Na, Mg, Al, P, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Ag, Ba, Ti). Calibration was performed using multi-element standards with Rh and In as internal standards for drift correction.

Results and Discussion

The analytical characteristics of the initial licorice meal are summarized in Table 1.

Table 2 presents the results of the mass spectrometric (ICP-MS) analysis of the ash obtained from licorice meal. The data indicate that licorice meals contain a diverse range of microelements that are essential for plant growth and physiological development.

Under the optimal oxidation conditions, the degree of oxidation of the licorice meal reached 70.94%. The resulting oxidation product consisted of 87.78% organic matter, including 35.88% humic acids, 26.39% fulvic acids, and 29.06% residual unoxidized meal. This wet, dense oxidized mass was subsequently used as the starting material for processing the decomposition products of phosphate raw materials.

The functional groups of the initial licorice meal, the oxidized meal, the residual unoxidized fraction, and the humic acids (HA) isolated from both the original and oxidized material were determined. The analytical results are summarized in Table 3.

Table 1 - Chemical composition of the original licorice root meal

Humidity, %	**Ash content, %**	**Content of extractive substances extracted by 1% NaOH solution, %**	**Content of extractive substances extracted by water, %**	**Insoluble organic matter, %**
5.41	4.66	5.87	15.78	68.28

Table 2 - Results of mass spectrometric analysis of licorice meal ash

Name and content of elements, in g/t									
Li	Be	B	Na	Mg	Al	P	K	Ca	Cr
59	1.80	16	12000	14000	80000	770	21000	65000	55
Mn	Fe	Co	Ni	Cu	Zn	Mo	Ag	Ba	Ti
1200	34000	16	40	75	100	3.30	0.490	440	3600

Table 3 - Active functional groups of the original licorice meal and its oxidation products

Substance	Moisture, %	Ash, %	Functional groups		
			COOH+OH, mg-eq/g	COOH, mg-eq/g	OH, mg-eq/g
Original meal	5.41	4.66	5.75	2.56	3.19
Oxidized meal	4.60	1.18	8.41	3.4	5.01
Humic acids of original meal	2.01	0.69	9.79	5.0	4.79
Humic acids of oxidized meal	3.83	0.63	10.66	5.02	5.64
Residual organic matter of original meal	5.34	6.04	2.53	1.18	1.35
Residual organic matter of oxidized meal	5.11	6.76	2.99	1.18	1.81

As shown in Table 3, oxidation of licorice meal with hydrogen peroxide in the presence of acetic acid significantly increased the content of active functional groups in both the oxidized material and the humic acids derived from it. In the original meal, the carboxyl group content was 2.56 mg-eq/g and the phenolic hydroxyl content was 3.19 mg-eq/g. After oxidation, these values increased to 3.40 mg-eq/g and 5.01 mg-eq/g, respectively. Even more pronounced changes were observed in the humic acids isolated from the oxidized meal, in which the carboxyl and phenolic hydroxyl group contents reached 5.00 mg-eq/g and 4.79 mg-eq/g, respectively. These results confirm that oxidative treatment enhances the reactivity and functional group enrichment of licorice-derived organic matter, improving its potential suitability for producing humic fertilizers.

The analytical results are presented in Tables 4–5.

Table 4 - Composition of phosphorus-humus fertilizers obtained based on oxidized meal with hydrogen peroxide and phosphorite powder from the Kyzylkum deposit in Uzbekistan

Ratio of Phosphorite: meal	P_2O_5 total, %	P_2O_5 accep by 2% citric acid, %	P_2O_5 accep. 0.2 M EDTA%	CaO total, %	$\frac{P_2O_{5accep.}}{P_2O_{5total}}$, %	SO_3 total, %	N total, %	OS, %	ES, %
Stoichiometric consumption of H_2SO_4 requirement for $Ca(H_2PO_4)_2$ formation (40%)									
1 : 0	14.75	5.93	4.40	41.52	40.26	30.34	0.60	0	0
1 : 0.2	13.02	5.67	4.14	37.08	43.58	26.80	0.77	14.35	10.18
1 : 0.4	11.35	5.30	3.87	32.26	46.75	24.11	0.89	25.07	17.78
1 : 0.6	9.68	4.71	3.20	28.67	48.62	21.37	1.10	33.11	23.48
1 : 0.8	8.83	4.46	2.76	25.54	50.53	19.56	1.24	39.31	27.88
1 : 1.0	7.91	4.15	2.38	22.89	52.44	17.32	1.37	44.16	31.32
Stoichiometric consumption of H_2SO_4 requirement for $Ca(H_2PO_4)_2$ formation (50%)									
1 : 0	14.19	7.08	5.87	40.00	49.89	29.88	1.10	0	0
1 : 0,2	12.57	6.57	5.38	35.66	52.27	26.23	1.36	13.90	9.86
1 : 0,4	10.98	6.05	4.96	31.25	55.14	23.75	1.54	24.72	17.53
1 : 0,6	9.33	5.26	4.18	27.53	56.48	20.96	1.66	32.76	23.24
1 : 0,8	8.35	4.83	3.70	24.38	57.87	19.12	1.83	38.91	27.60
1 : 1,0	7.68	4.56	3.21	22.27	59.41	16.80	1.98	43.85	31.10
Stoichiometric consumption of H_2SO_4 requirement for $Ca(H_2PO_4)_2$ formation (60%)									
1 : 0	13.47	8.02	6.34	38.04	59.56	29.37	1.50	0	0
1 : 0.2	11.93	7.33	5.97	33.85	61.44	25.78	1.83	13.38	9.49
1 : 0.4	10.52	6.67	5.23	30.25	63.58	23.04	1.97	24.11	17.03
1 : 0.6	9.05	5.84	4.38	26.20	64.52	20.26	2.12	31.93	22.46
1 : 0.8	7.84	5.13	3.86	23.57	65.49	18.66	2.29	38.44	27.26
1 : 1.0	7.45	4.94	3.35	21.64	66.42	16.39	2.45	43.38	30.77
Stoichiometric consumption of H_2SO_4 requirement for $Ca(H_2PO_4)_2$ formation (70%)									
1 : 0	12.94	8.93	7.41	36.58	69.05	28.77	2.21	0	0
1 : 0.2	11.76	8.31	6.98	31.65	70.66	24.96	2.37	12.92	9.16
1 : 0.4	10.25	7.38	5.85	29.27	72.00	22.45	2.56	23.75	16.59
1 : 0.6	8.77	6.56	4.67	25.62	72.48	19.80	2.72	31.44	21.95
1 : 0.8	7.53	5.49	4.11	22.76	72.93	18.06	2.98	37.91	26.89
1 : 1.0	6.96	5.11	3.72	21.02	73.45	15.93	3.14	42.84	30.39
Stoichiometric consumption of H_2SO_4 requirement for $Ca(H_2PO_4)_2$ formation (80%)									
1 : 0	12.41	10.14	8.56	35.20	78.54	28.12	2.48	0	0
1 : 0.2	11.38	9.06	7.43	30.33	79.61	24.56	2.65	12.43	8.82
1 : 0.4	9.89	8.36	6.27	28.28	80.46	21.87	2.83	23.11	16.39
1 : 0.6	8.33	6.73	5.04	24.57	80.87	19.36	2.99	30.89	21.91
1 : 0.8	7.11	5.78	4.68	22.06	81.34	17.68	3.14	37.21	26.40
1 : 1.0	6.49	6.12	4.11	20.39	81.72	15.56	3.32	41.93	29.74

Table 5 - Composition of phosphorus-humus fertilizers obtained on the basis of oxidized meal with hydrogen peroxide and phosphorite powder from the Durnals deposit in Turkmenistan

Ratio of Phosphorite : meal	P_2O_5 total, %	P_2O_5 accep by 2% citric acid, %	P_2O_5 accep. 0.2 M EDTA%	CaO total, %	$\frac{P_2O_{5accep.}}{P_2O_{5total}}$, %	SO_3 total, %	N total, %	OS, %	ES, %
Stoichiometric consumption of H_2SO_4 requirement for $Ca(H_2PO_4)_2$ formation (10%)									
1 : 0	13.46	6.47	4.39	28.01	48.08	22.88	0.61	0	0
1 : 0.2	11.52	5.77	3.93	22.63	50.13	18.75	0.68	17.93	12.72
1 : 0.4	9.93	5.20	3.64	19.57	52.35	15.62	0.76	28.37	20.12
1 : 0.6	9.25	5.01	3.35	17.11	54.17	13.14	0.87	36.51	25.90
1 : 0.8	8.57	4.84	3.11	15.38	56.53	11.42	0.95	43.15	30.61
1 : 1.0	7.86	4.57	2.88	14.23	58.19	9.79	1.08	47.82	33.92
Stoichiometric consumption of H_2SO_4 requirement for $Ca(H_2PO_4)_2$ formation (20%)									
1 : 0	13.34	6.90	4.85	27.75	51.77	23.91	1.01	0	0
1 : 0.2	11.28	5.99	4.06	22.32	53.18	19.46	1.12	17.36	12.31
1 : 0.4	9.61	5.32	3.69	19.24	55.32	16.28	1.23	27.73	19.67
1 : 0.6	8.42	4.85	3.27	16.85	57.61	13.87	1.31	35.85	25.43
1 : 0.8	7.91	4.73	3.15	14.97	59.83	12.02	1.39	42.32	30.02
1 : 1.0	7.53	4.64	2.97	13.86	61.58	10.45	1.51	47.06	33.38
Stoichiometric consumption of H_2SO_4 requirement for $Ca(H_2PO_4)_2$ formation (30%)									
1 : 0	13.18	7.96	5.15	27.56	60.43	25.17	1.45	0	0
1 : 0.2	11.05	6.92	4.28	22.07	62.66	20.05	1.61	16.68	11.83
1 : 0.4	9.37	6.03	3.91	18.92	64.37	16.92	1.70	27.10	19.22
1 : 0.6	8.22	5.48	3.52	16.51	66.75	14.56	1.82	35.12	24.91
1 : 0.8	7.81	5.35	3.28	14.75	68.51	12.73	1.93	41.77	29.63
1 : 1.0	7.27	5.12	3.11	13.56	70.44	11.15	2.07	46.36	32.89
Stoichiometric consumption of H_2SO_4 requirement for $Ca(H_2PO_4)_2$ formation (40%)									
1 : 0	12.96	9.09	5.27	27.25	70.17	26.04	2.10	0	0
1 : 0.2	10.77	7.83	4.60	21.62	72.68	20.72	2.19	15.87	11.26
1 : 0.4	9.02	6.70	4.22	18.51	74.32	17.64	2.32	26.20	18.64
1 : 0.6	7.84	6.13	3.82	16.12	78.17	15.30	2.40	34.28	24.32
1 : 0.8	7.43	5.93	3.47	14.38	79.83	13.44	2.55	40.85	28.98
1 : 1.0	6.82	5.56	3.20	12.93	81.52	11.88	2.66	45.62	32.36
Stoichiometric consumption of H_2SO_4 requirement for $Ca(H_2PO_4)_2$ formation (50%)									
1 : 0	12.73	10.20	5.69	26.98	80.17	27.04	2.46	0	0
1 : 0.2	10.40	8.56	4.94	21.38	82.35	21.42	2.58	15.16	10.75
1 : 0.4	8.91	7.51	4.47	18.31	84.32	18.34	2.75	25.46	18.41
1 : 0.6	7.76	6.79	3.95	15.94	87.53	15.95	2.84	33.91	23.99
1 : 0.8	6.87	6.12	3.58	14.11	89.07	14.14	2.96	40.01	28.38
1 : 1.0	6.16	5.58	3.21	12.65	90.64	12.68	3.11	44.85	31.82

The results obtained for both types of phosphate raw materials demonstrated similar trends. As the sulfuric acid dosage increased and the proportion of phosphate raw material decreased, the total P_2O_5 content (P_2O_{5total}) of the final product decreased; however, the relative proportion of plant-available phosphorus ($P_2O_{5assimilable}$) increased. This indicates that higher acidification promotes deeper decomposition of the phosphate phase and conversion of P_2O_5 into more soluble forms.

At a meal-to-phosphorite ratio of 1: 0.2 and a sulfuric acid rate of 40% of the stoichiometric requirement for monocalcium phosphate formation, the resulting phosphorus–humus fertilizer contained (wt.%):P_2O_{5total} – 13.02; $P_2O_{5citric\text{-}soluble}$ – 5.67; $P_2O_{5byTrilon\ B\text{-}soluble}$ – 4.14; organic

substance (OS) – 14.35; extractive substance (ES) – 10.18; nitrogen – 0.77; CaO_{total} – 37.08. The relative content of citric-soluble P_2O_5 was 43.58% of P_2O_{5total}.

Increasing the acid dosage to 80% of stoichiometry at the same meal-to-phosphorite ratio resulted in a fertilizer with the following composition (wt.%): P_2O_{5total} – 11.38; $P_2O_{5citric\text{-}soluble}$ – 9.06; $P_2O_{5byTrilon\ B\text{-}soluble}$ – 7.43; OS – 12.43; ES – 8.82; nitrogen – 2.65; CaO_{total} – 30.33. The relative content of P_2O_5 available to plants, determined using citric acid, is 79.61, indicating that the relative available form of phosphorus increases by approximately 2-fold.

Based on the data presented in Tables 4 and 5, it can be observed that the presence of humic acids in the oxidized meal increases the relative content of plant-available P_2O_5 by 1.5–10% compared with phosphate rock digestion carried out in the absence of oxidized organic matter. Unlike previous studies, the present research clearly demonstrates that humic substances significantly enhance the relative availability of phosphorus in the resulting products, which in turn enables a reduction in sulfuric acid consumption and decreases the amount of phosphogypsum waste generated per ton of finished fertilizer.

From the data in Table 4, it can be seen that with an increase in the amount of oxidized meal, plant-available phosphorus increases. When the phosphorus to meal ratio is 1 : 0 and with 40% stoichiometric dosage of sulfuric acid for monocalcium phosphate, the content of P_2O_5 in digestible form increases to 40.26%. When the phosphorus-to-meal ratio is altered to 1:1 with continued use of 40% stoichiometric dosage of sulfuric acid, this content increases to 52.44%, solidifying the fact that oxidized organic matter has a positive influence on phosphorus solubilization.

Similar observations were also realized when phosphate rock from the Turkmenistan Deposit was used (Table 5). For example, at a meal-to-phosphorite ratio of 1: 0.4 and a sulfuric acid rate of 10% of stoichiometry, the resulting humic superphosphate exhibited the following composition (wt.%): P_2O_{5total} – 9.93; $P_2O_{5citric\text{-}soluble}$ – 5.20; $P_2O_{5\ byTrilon\ B\text{-}soluble}$ – 3.64; OS – 28.37; ES – 20.12; nitrogen – 0.76; CaO_{total} – 19.57.

Under these conditions, the relative proportion of citric-soluble P_2O_5 reached 52.35%.

Increasing the sulfuric acid dosage to 50% of stoichiometry at the same meal-to-phosphorite ratio yielded a product with the following composition (wt.%):

P_2O_{5total} – 8.91; $P_2O_{5citric\text{-}soluble}$ – 7.51; $P_2O_{5\ byTrilon\ B\text{-}soluble}$ – 4.47; OS – 25.46; ES – 18.41; nitrogen – 2.75; CaOtotal – 18.31.

The relative content of citric-soluble P_2O_5 increased sharply to 84.32%, demonstrating a substantial improvement in phosphorus availability at higher degrees of phosphate decomposition.

These results collectively confirm that both the oxidized organic component and the acid decomposition level are key factors governing the formation of readily assimilable phosphorus forms in phosphorus–humus fertilizers.

Figures 1–4 present the X-ray diffraction (XRD) patterns of the initial phosphate raw materials from the Central Kyzylkum Desert (Uzbekistan) and Turkmenistan, along with the diffraction profiles of the phosphorus–humus fertilizers produced at a phosphorite-to-meal ratio of 1: 1 and a sulfuric acid dosage of 50% of the stoichiometric requirement for monocalcium phosphate formation. The comparative XRD analysis enables identification of phase transformations occurring during acid decomposition and subsequent interaction with oxidized organic matter.

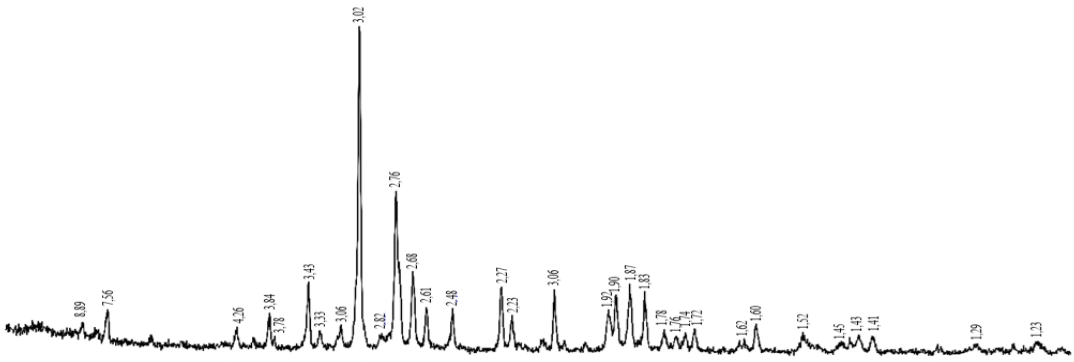

Figure 1 - XRD of phosphate rock from the Kyzylkum deposit in Uzbekistan

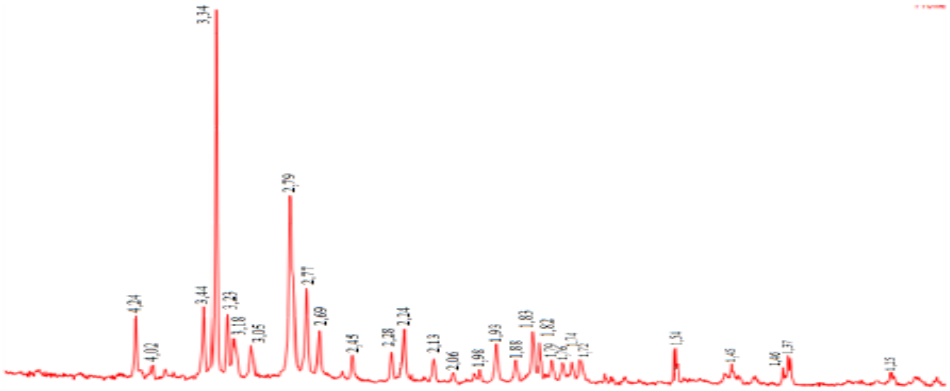

Figure 2 - XRD of phosphate rock from the Durnals deposit in Turkmenistan

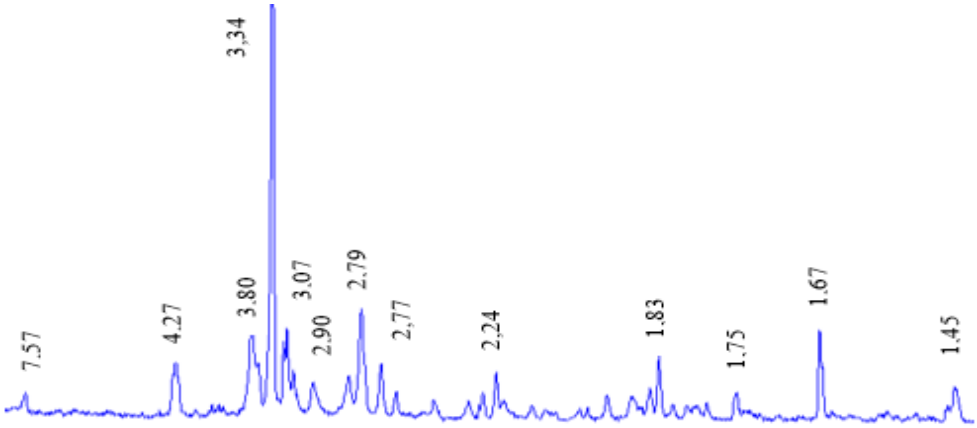

Figure 3 - XRD of phosphorus-humus fertilizer obtained from phosphate raw materials of the Kyzylkum deposit in Uzbekistan

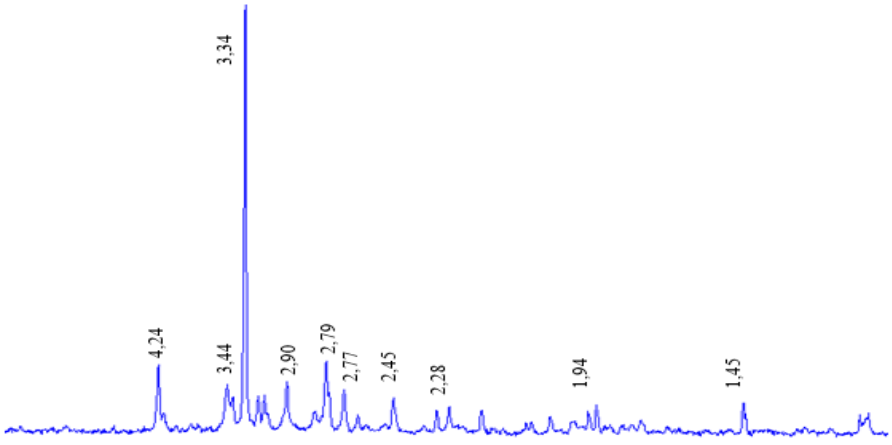

Figure 4 - XRD of phosphorus-humus fertilizer obtained from phosphate raw materials of the Durnals deposit in Turkmenistan

In the XRD of phosphate rock from the Kyzylkum deposit (Uzbekistan) (Fig. 1), the characteristic reflections at 1.72, 1.74, 1.79, 1.83, 1.93, 2.24, 2.69, 2.77, 2.79, 3.18, and 3.44 Å correspond to fluorocarbonate–apatite, the principal phosphate-bearing phase. The presence of calcite is confirmed by diffraction lines at 1.88, 2.28, and 3.05 Å, while reflections at 1.37, 1.54, and 4.02 Å indicate dolomite. Strong peaks at 1.82, 1.98, 2.13, 2.45, 3.23, 3.34, and 4.24 Å reflect a significant contribution from silicon oxide (SiO_2). Additional bands at 1.37 and 1.94 Å are attributed to calcium

fluoride (CaF_2), whereas lines at 2.06, 2.45, and 3.23 Å can be assigned to calcium silicate ($CaSiO_3$).

In the XRD of phosphate rock from the Turkmenistan deposit (Fig.2), the reflections at 1.72, 1.74, 1.79, 1.83, 1.93, 2.24, 2.69, 2.77, 2.79, 3.18, and 3.44 Å correspond to fluorocarbonate apatite, confirming its role as the primary phosphate mineral. The presence of calcite is indicated by peaks at 1.88, 2.28, and 3.05 Å, while reflections at 1.37, 1.54, and 4.02 Å signify dolomite. Strong peaks at 1.82, 1.98, 2.13, 2.45, 3.23, 3.34, and 4.24 Å confirm a high concentration of silicon oxide (SiO_2). Peaks at 1.37 and 1.94 Å are characteristic of calcium fluoride (CaF_2). Peaks at 2.06, 2.45, and 3.23 Å confirm the presence of calcium silicate ($CaSiO_3$)

In the XRD pattern of the phosphorus-humus fertilizer based on the Kyzylkum phosphate rock phosphates (Fig. 3), the process of chemical degradation with sulfuric acid and the addition of oxidized meal led to the occurrence of distinct changes in the structure. This pattern shows the characteristic peaks of monocalcium phosphate at 3.80, 2.79, and 2.21 Å; and those of dicalcium phosphate and tricalcium phosphate at 3.50 and 2.66 Å and 3.44 Å, respectively. Peaks due to ammonium sulfate appear at 2.32 Å, and gypsum at 1.45 Å.

The XRD pattern of the phosphorus-humus fertilizer obtained from the phosphate rock in Turkmenistan (Fig.4) has the same mineral composition. The peaks due to monocalcium phosphate are present at 7.57 Å, 2.90 Å, 1.83 Å, and 1.65 Å, while for dicalcium phosphate at 1.75 Å. The peaks due to ammonium sulfate at 2.32 Å and gypsum at 1.45 Å have also been identified. The diffraction pattern shows that the acidification process and the formation of humus have resulted in the formation of soluble phosphate materials in all phosphate rocks.

Worth noting here is that, during the manufacture of phosphate fertilizers, the ammoniation and drying stages usually entail a corresponding decline in available P_2O_5 content due to phosphorus retrogradation. Nevertheless, adding the oxidized meal to the phosphate raw materials significantly raises the level of available P_2O_5 content. This appears to be related to the presence of organic acids in the oxidized meal, which, when reacting with monocalcium phosphate and other phosphates in the acidic superphosphate mixture, retard phosphorus retrogradation reactions (Eqs 2-6). As such, contrary to expectations, rather than decreasing, there would be a substantially augmented level of available phosphorus content following the ammoniation stage instead.

According to contemporary agriculture requirements, the comparative number of phosphoric acids in complex fertilizer should not be lower than 50% as compared to the total amount of fertilizer. Using this data, the best conditions for processing phosphate rock from the Kyzylkum deposit (Uzbekistan) were calculated. The best results were attained for sulfuric acid amount 70% from stoichiometry for monocalcium phosphate and ratio of phosphorite to oxidized meal 1 to 0.6.

Under these optimized conditions, the resulting granular fertilizer exhibited the following composition (wt.%): P_2O_{5total} – 8.77; $P_2O_{5citric\text{-}acid\text{-}soluble}$ – 6.56; OS – 31.44; HA – 21.95; nitrogen – 2.72; CaO_{total} – 25.62; relative content of citric-acid-soluble P_2O_5 – 72.48%; moisture – 5.17; and total SO_3 – 19.80. The mechanical strength of the granules reached 2.3 MPa, which is sufficient for storage, transportation, and field application. These results confirm that the introduction of oxidized meal under the selected process conditions allows for the production of a phosphorus–humus fertilizer with a high proportion of assimilable P_2O_5 and improved physical properties.

For the processing of phosphate rock from Turkmenistan, the optimal technological parameters were established as follows: a sulfuric acid dosage equal to 40% of the stoichiometric requirement for monocalcium phosphate formation and a phosphorite-to-oxidized-meal mass ratio of 1:0.6. Under these conditions, the resulting phosphorus–humus fertilizer had the following composition (wt.%): P_2O_{5total} – 7.84; $P_2O_{5citric\text{-}acid\text{-}soluble}$ – 6.13; OS – 34.28; HA – 24.32; nitrogen – 2.40; CaO_{total} – 16.12; relative content of citric-acid-soluble P_2O_5 – 78.17%; moisture – 5.62; and total SO_3 – 15.30. The granules exhibited a mechanical strength of 2.4 MPa, indicating sufficient durability for handling, transport, and field application.

These results demonstrate that the selected conditions for Turkmenistan phosphate rock ensure a high proportion of plant-available P_2O_5 and enhanced fertilizer quality, comparable to or exceeding typical requirements for complex fertilizers.

Based on the conducted research, the key technological parameters for the production of phosphorus–humus fertilizers from phosphate rock of the Kyzylkum deposit (Uzbekistan) and Durnals deposit (Turkmenistan) were established, and the material flows and a basic technological scheme were developed (Figs. 5–7).

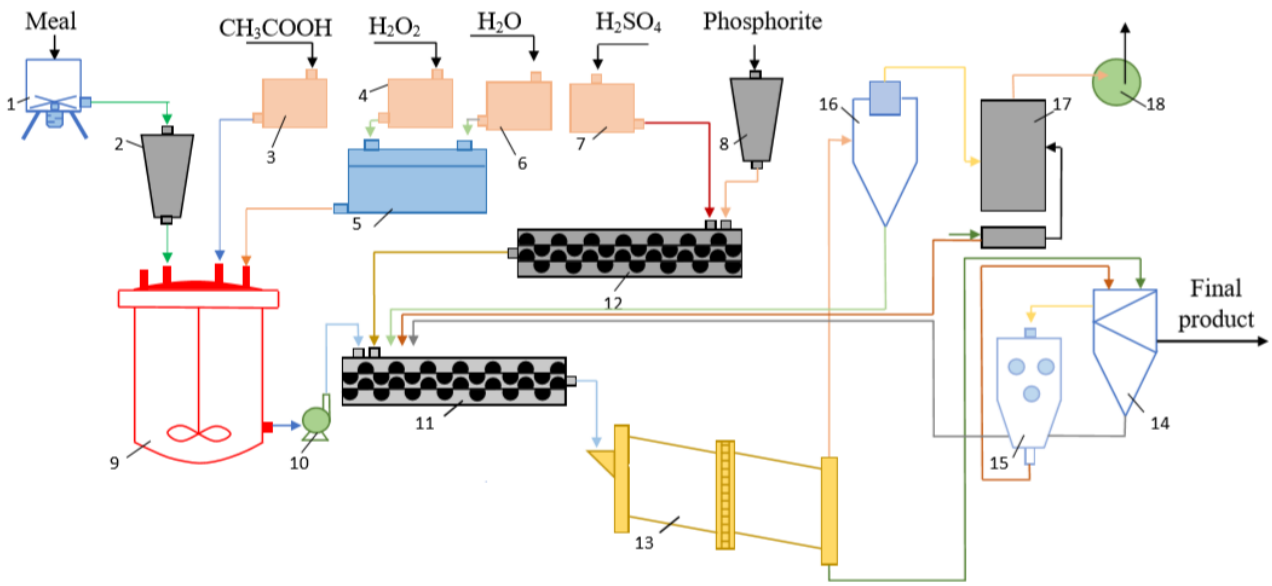

Figure 5 - Basic technological flow sheet for the production of phosphorus–humus fertilizer: 1 – knife crusher; 2,8 - feeder hopper; 3,4,6,7- tanks; 5 - automatic concentrator; 9 - reactor; 10 -pump; 11, 12 - auger mixer; 13 - drum dryer; 14 – classifier; 15-crusher 16 -cyclone; 17-scrubber; 18 – fan.

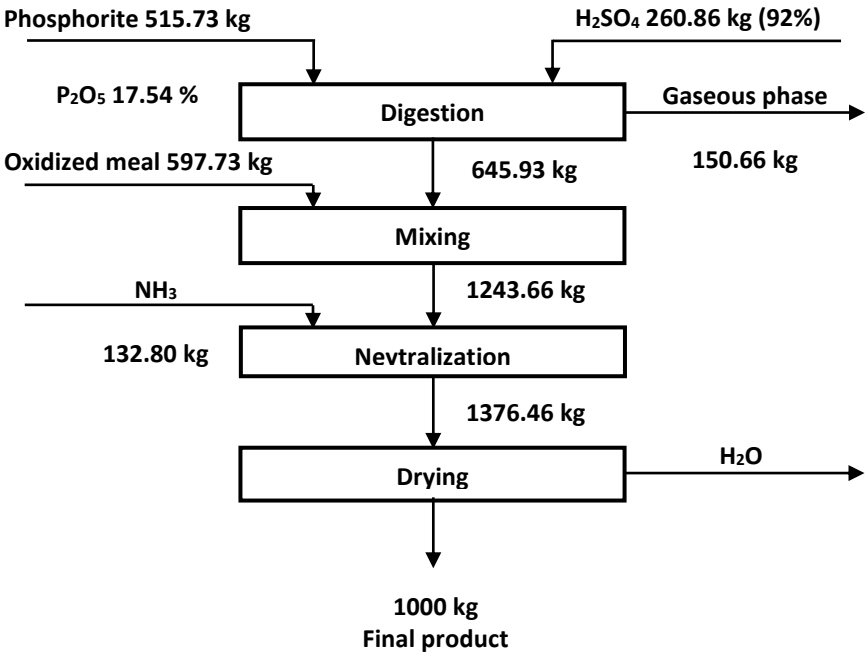

Figure 6 - Material balance for the production of phosphorus–humus fertilizer from phosphate rock sourced from the Kyzylkum deposit, Uzbekistan.

The optimal process conditions for producing humic simple superphosphate are as follows: grinding of licorice meal to a particle size below 0.25 mm; hydrogen peroxide concentration of 10%; mass ratio of the organic portion of licorice meal to H_2O_2 and acetic acid of 100:1:0.1; sulfuric acid dosage for decomposition of Kyzylkum phosphate rock to $Ca(H_2PO_4)_2$ of 60% of the stoichiometric requirement, and for Turkmenistan phosphate rock, 40% of the stoichiometric requirement; mass ratio of organic meal to phosphorite of 1:0.4; oxidation temperature of 60°C and duration of 60 min; phosphorite decomposition time of 30 min; neutralization of the resulting pulp with ammonia to pH 4.5 for 20 min; and drying of the final product at 80–100°C.

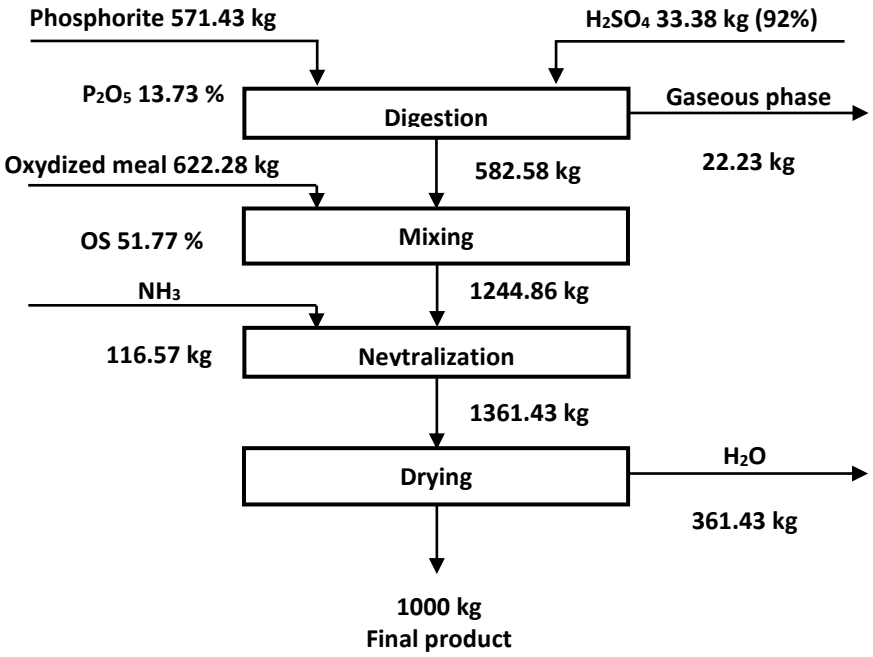

Figure 7 - Material balance for the production of phosphorus–humus fertilizer from phosphate rock sourced from the Durnals deposit, Turkmanistan.

Hydrogen peroxide (60%) is pumped from the storage tank (1) to the pressure tank (3) and subsequently to the automatic concentrator (5), where it is diluted to 10% with water. The diluted oxidizer is then fed to the reactor (8) together with crushed licorice meal (2) for oxidation.

The phosphate rock is treated with sulfuric acid in the two-shaft screw reactor (10). The obtained acid superphosphate is passed on to the screw mixer (11), where it is mixed with the oxidized licorice meal, recycled, and the 25% ammonia solution for neutralization.

The homogeneous mixture is then moved to the drum dryer (12) for drying and then to the screening unit (16) for granule classification. Off-gases with ammonia and dust are purified in a cyclone (13) and a water scrubber (14) and then emitted into the atmosphere.

Finally, dried and screened granules are transported to the classification unit and subsequently warehoused in the finished product warehouse.

Compared with these existing methods, the present technology combines partial sulfuric acid decomposition of low-grade phosphate rock with oxidized licorice meal, achieving high proportions of plant-available P_2O_5 (up to 78–84%) while reducing sulfuric acid consumption to 40–60% of the stoichiometric requirement. In addition, the resulting granular fertilizers exhibit sufficient mechanical strength for storage and field application, addressing both agronomic efficiency and logistical practicality.

Overall, by overcoming the high material demand, long processing time, and technological complexity associated with previously reported methods [[11], [12], [13],[14], [15]], the proposed approach offers a more efficient and scalable route for producing phosphorus–humus fertilizers suitable for modern agricultural systems.

Conclusion

The effects of oxidizer concentration, temperature, and the weight ratio of the organic portion of the meal to anhydrous hydrogen peroxide were taken into consideration for improving the humic substances and organic acids content in licorice meal through oxidation with hydrogen peroxide in the presence of acetic acid. The oxidized meal was characterized by its humic substance content and functional groups. A technology has also been developed in this work on the production of phosphorus–humus fertilizers by incorporating the oxidized meal into the acidic superphosphate mass before ammoniation and drying. This treatment simultaneously increases the relative content of digestible P_2O_5 forms and decreases the sulfuric acid requirement for phosphate decomposition. The application of such fertilizers in

agriculture is expected to improve the soil humus content and to ameliorate the structure and physical–mechanical properties of the soil, ensuring the complete supply of all essential plant nutrients, which will result in increased yields, improved crop quality, and an enhancement in resistance to diseases.

Conflicts of interest. On behalf of all authors, the corresponding author states that there is no conflict of interest.

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АННОТАЦИЯ

Гумус құрамды органикалық және органо-минералдық тыңайтқыштар жоғары су ұстау қабілетінің, жақсартылған су өткізгіштігінің, сондай-ақ карбонатты топырақтарда кальций мен магний иондарының және қышқыл топырақтарда сесквиоксидтердің әсерінен фосфордың фиксациясын төмендету қасиетінің арқасында топырақ құнарлылығын арттыруда маңызды рөл атқарады. Мал шаруашылығы қалдықтарынан, шымтезектен және қоңыр көмірден алынған органикалық заттар тыңайтқыштарды гумуспен байытуға мүмкіндік береді. Алайда өсімдік қалдықтары, атап айтқанда көктерек қабығы, ауыл шаруашылығы қалдықтарының қауыздары және мия тамырының ұны, органикалық тыңайтқыштар өндіру үшін ең тиімді қоспалардың қатарына жатады. Бұл зерттеуде Түрікменстандағы Қызылқұм кен орнынан табылған индикаторлы фосфориттер мен сутек асқын тотығы және сірке қышқылымен өңделген тотықтырылған мия пастасын пайдалана отырып, түйіршіктелген фосфор-гумусты тыңайтқыштарды синтездеу бағаланды. Зертханалық эксперимент әдістемесі үш кезеңнен тұрды. Бірінші кезеңде бөлшек өлшемі < 0,1 мм болатын ұсақталған мия ұнының тотығу қасиеттері судағы сутек асқын тотығы ерітіндісі мен сірке қышқылы арқылы, мияның органикалық фракциясына қатысты H_2O_2 : CH_3COOH = 100 : (10–20) : (0,1–1) массалық қатынастарында зерттелді. Екінші кезеңде фосфорит 92%-дық күкірт қышқылымен монокальцийфосфат түзілуіне қажетті стехиометриялық мөлшердің 30–80%-ы көлемінде ыдыратылды. Үшінші кезеңде алынған өнімдер тотықтырылған мия пастасымен 100:10:1 қатынасында араластырылды. Жұмыста фосфор-гумусты тыңайтқыштарды өндеудің оңтайлы шарттары бағаланып, әрбір шикізат көзіне сәйкес технологиялық ағындық сызбалар әзірленді. Ұсынылған жаңа технологияның тиімділігі көрсетілді. Алынған нәтижелер төмен сапалы фосфориттер мен мия тамыры қалдықтарының экологиялық тұрғыдан қауіпсіз екенін және жоғары шығынды химиялық тыңайтқыштарды қолдануды немесе уақытты көп қажет ететін дәстүрлі компосттау процестерін азайту үшін баламалы құрал ретінде пайдалануға болатынын көрсетті.

Түйін сөздер: мия тамыры ұны, сутек асқын тотығы, фосфорит, экстрактивті заттар, күкірт қышқылы, тотығу

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АННОТАЦИЯ

Гумуссодержащие органические и органо-минеральные удобрения играют ключевую роль в повышении плодородия почв благодаря их высокой влагоудерживающей способности, улучшенной водопроницаемости, а также способности снижать фиксацию фосфора ионами кальция и магния в карбонатных почвах и сесквиоксидами в кислых почвах. Органическое вещество, получаемое из отходов животноводства, торфа и бурого угля, может обогащать удобрения гумусом. Однако растительные остатки, такие как кора осины, сельскохозяйственные шелухи и мука из корня солодки, относятся к числу наиболее эффективных добавок для производства органических удобрений. В настоящем исследовании оценивался синтез фосфорно-гумусных удобрений в гранулированной форме с использованием индикаторных фосфоритов, обнаруженных в месторождении Кызылкум (Туркменистан), а также окисленной пасты корня солодки, обработанной перекисью водорода и уксусной кислотой. Лабораторная методика эксперимента включала три этапа. На первом этапе изучалось окислительное поведение тонкоизмельчённой муки солодки (размер частиц < 0,1 мм) с использованием водного раствора перекиси водорода и уксусной кислоты при массовых соотношениях по отношению к органической фракции солодки в диапазоне H_2O_2 : CH_3COOH = 100 : (10–20) : (0,1–1). На втором этапе фосфорит подвергался разложению 92%-ной серной кислотой в количестве 30–80 % от стехиометрически необходимого для образования монокальцийфосфата. На третьем этапе полученные продукты смешивали с окисленной пастой солодки в соотношении 100:10:1. В работе оценены оптимальные условия переработки фосфорно-гумусных удобрений, а также разработаны технологические схемы переработки, включая фосфатное сырьё, поступающее из каждого источника. Представлена эффективность новой технологии. Полученные результаты показывают, что низкосортные фосфориты и отходы корня солодки являются экологически безопасными и могут быть рекомендованы в качестве альтернативного инструмента для снижения использования высокозатратных химических удобрений или трудоёмких традиционных процессов компостирования.

Ключевые слова: мука из корня солодки, перекись водорода, фосфорит, экстрактивные вещества, серная кислота, окисление

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