Obtaining complex fertilizers based on low-grade phosphorites

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Abstract. In the study, the process preparation of phosphorus-humus fertilizers based on low-grade Central Kizilkum phosphorites activated using sulfuric acid in the ratio of 30-70% for decomposition of CaCO3 in the phosphorite followed by addition of activated sludge from municipal waster water was investigated.

1 Introduction

It should be noted that at present, the main problems of agricultural production in many countries of the world, including the Republic of Uzbekistan, are the lack of especially phosphate fertilizers, a decrease in the content of humus in soils and salinization of soils; these problems can be solved to some extent by organizing large-scale production and application organic fertilizer.

Humus is the major composite of soil determining its property and fertility. The significance of humus in a soil is vast. Humus improves soil's chemical, physical and biological properties promoting the generation of strong structure that provides plant by nitrogen and other substances in exposed form during the mineralization. It should be noted that livestock farm's manure is the main source of organic matter for the reproduction of humus in agriculture [1-4]. The main value of manure as a fertilizer is the content of more nitrogen and carbon, which can increase the growth of the crop in a span of manure application. Carbon-based material supplies or grows the humus content of humus in the soil, therefore, piling soil fertility in the future. In that case, after application, manure works in the soil for some years that is as a fertilizer with prolonged activation [5-7].

There is a lot of information on the advantages of organic fertilizers over mineral fertilizers in the literature. So, at work [8-10], it is reported that the greatest effectiveness of organic and mineral fertilizers is achieved when they are used together, that is, the creation of organic fertilizers. In cotton-growing, a highly effective method is the joint application of organic and mineral fertilizers. Its advantage is due to the temporary biological fixation of nutrients of mineral fertilizers by microorganisms with their subsequent release in an accessible form for plants. This process reduces the movement of nitrogen into the deep horizons of the soil and the removal of the surface layer, resulting in improved nitrogen and

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phosphorus nutrition of plants. The experiments conducted at the Uzbek Research Institute of Cotton Production showed that the cotton crop (on average over five years) amounted to: from mineral fertilizers - 50.2 c/ga, manure - 38.8, and when applied together - 53.5 c/ga [11].

In work [12], it is noted that only organic fertilizers, when used together with mineral fertilizers, can ensure a deficit-free balance or an increase in humus in typical crop rotation zones. These words are confirmed by the experience in the Grodno region (Belarus), where the use of organic fertilizers on sod-podzolic soil increased over 60 years the humus reserves in the 0-150 cm layer by 21- 24% compared with the control and by 49% with the virgin soil [13]. In the experiments of Fokin A.D. the plant utilization rate of phosphorus from decaying plant residues was more than 4 fold higher than that of mineral fertilizers [14]. With a high content of humus in the soil due to more favorable agrophysical properties and improved conditions for the development of plants, the return on mineral fertilizers increases by 1.5-2 folds. Infield experiments of the Belarusian Research Institute of Soil Science and Agrochemistry, a change in the amount of humus in sod-podzolic soil from 1.5 to 2.5-3% led to a 3-fold increase in the efficiency of 1 kg NPK fat [15].

Raw materials for organic and organic fertilizers include litter manure, litter less manure, bird droppings, peat, brown coal, green manure, straw, sapropel, household and industrial waste, and sewage sludge [16].

As already noted, currently, in many countries of the world, there is a decrease in the resources of phosphate raw materials. In 2018, enterprises of Uzkimyosanoat JSC of the Republic of Uzbekistan produced 153.8 thousand tons of phosphate fertilizers (in terms of 100% P_2O_5). In contrast, the need for agriculture is 691.7 thousand tons of P_2O_5. These figures indicate that the availability of phosphate fertilizers in agriculture is insufficient. Currently, at the Kyzylkum phosphorite plant, when highly carbonized phosphorites of the Central Kyzyl Kum are enriched, waste is generated in the form of a mineralized mass with 13-15% content P_2O_5 and sludge phosphorites with a content of 8-12% P_2O_5. The total volume of accumulated waste phosphorites has already reached 15 million tons. With a drawback of phosphate fertilizers, these waste phosphorites can serve as a large reserve to increase the production of phosphate fertilizers. Conventional phosphate processing methods, such as nitric acid and sulfuric acid, are not acceptable to them. Alternative to traditional acidic methods for the production of phosphate fertilizers can be alternative methods that use organic brown coal, animal waste, poultry and sewage sludge instead of strong mineral acids.

Based on the above mentioned, we carried out several studies on the production of organic fertilizers based on substandard phosphorites, cattle and poultry manure by composting and accelerated methods. It is shown that even from such waste phosphorites, such as mineralized mass and sludge phosphorite it is possible to obtain highly effective nitrogen-phosphorus-humic fertilizers [17-19].

In our previous work [20], the processes of obtaining organic fertilizers based on sewage sludge and sludge phosphorite were investigated. The combined processing of sewage sludge and sludge phosphorite made it possible to use activated sludge microorganisms to convert non-digestible forms of phosphorus of substandard phosphorites into an assimilable form for plants, since microorganisms contained in sewage sludge can use many minerals, including phosphate, for their growth and development, in addition to this, sewage sludge contains a significant amount of carboxylic acids that can bind calcium ions contained in partially decomposed mine phosphorites acid acids. Under the influence of organic acids formed during the decomposition of wastewater sludge, phosphorus, which is part of substandard phosphorites, passes from an unapproachable form into a digestible form for plants and thereby will show its fertilizing properties. Also, activated phosphorite with mineral acids binds $(NH_4)_2CO_3$, free NH_3 and other organic volatile organic substances into non-volatile forms, spreading an unpleasant odor into the environment.

2 Materials and methods

At this stage of the work, to study the processes of obtaining organic fertilizers, the wastewater sludge from the city of Navoi was used (wt.%): Moisture - 65.43; ash - 9.74; organic matter - 24.83; humic acids - 3.05; fulvic acids - 7.47; water-soluble organic substances - 2.13; P_2O_5 - 1.39; N 1.17; K_2O - 0.44; CaO - 4.14 [21].
To table 1 results of mass spectrometric analysis (ICP – MS) of sewage sludge ash. It follows from the table that the sewage sludge contains some trace elements necessary for the growth and development of plants. Mineralized mass (MM) was used as phosphate feedstock. Before use, it was ground to a particle size of 0.25 mm. The composition of MM is shown in table 2. from table 2 it is seen that MM is characterized by a low phosphorus content (8.76% P_2O_5), a high content of carbonates (19.72% CO_2) and a high value of calcium module (CaO: P_2O5 = 5.19).

Table 1. The results of mass spectrometric analysis of ash from sewage sludge of the city of Navoi

Name and content of elements, in g/t									
Composition of wastewater sludge ash									
Li 600	Si 100000	B 3000	Na 40000	Mg 30000	Al 80000	P 62310	K 32000	Ca 303608	Sr 2000
Mn 1000	Fe 11312	Co 80	Ni 130	Cu 1000	Zn 30	Mo 1.46	Ag 3.01	Hg 2.0	Ti 500

Table 2. The chemical composition of the mineralized mass

The content of components, weight. %								
P_2O_5	CaO	Al_2O_3	Fe_2O_3	MgO	F	CO_2	SO_3	i.r.
14.27	42.01	1.12	1.34	1.45	1.73	18.57	1.05	13.14

The chemical analysis of the sewage sludge of the city of Navoi, sludge phosphorite and their products was carried out by the following methods. Humidity was determined according to GOST 26712-85, ash content according to GOST 26714-85 and organic matter according to GOST 27980-80. The amount of the water-soluble fraction of organic substances extracted from the products with water was determined by filtration and evaporation in a water bath, drying the solid residue to a constant weight, and then burning it to determine the ash content and subtract it. Humic acids were isolated by treating the products with 0.1 N alkali solution followed by acidification of the solution with mineral acid [22]. The solid phase after the separation of alkali-soluble organic substances from it contains residual organic matter. It was thoroughly washed with distilled water, dried to constant weight, and the content of organic substances was determined. The difference between the amounts of alkali-soluble organic substances and humic acids gives us the content of fulvic acids. All P_2O_5 forms were determined by the gravimetric method by precipitation of the phosphate ion with a magnesia mixture in magnesium ammonium phosphate, followed by calcination of the precipitate 1000-1050°C according to GOST 20851.2-75. Assimilable forms of P_2O_5 were determined by solubility in both 2% citric acid and 0.2 M Trilon B. The determination of CaO was carried out complexometrically: by titration with a 0.05 N Trilon B solution in the presence of a fluorexon indicator.

For the decomposition of MM, sulfuric acid used with a concentration of 92%. The rate of sulfuric acid varied in the range of 30-70% of the stoichiometry for the decomposition of CaO phosphate feed. The experiments were carried out as follows; sulfuric acid was slowly poured into a glass reactor in which a sample of the phosphorite was located. The duration of the interaction of the components was 30 minutes, after which sewage sludge was added to the pulp, and stirring was continued for 60 minutes. Drying was carried out at 80°C until the moisture content in the finished product 10-15%. The processing of sulfuric acid decomposition products by sewage sludge was carried out in the range of weight ratios of sewage sludge to MM from 100: 10 to 100: 40. The results are shown in figures 1-3.

3 Results and Discussions

From fig. 1-3, it can be seen that the higher the norm of sulfuric acid and the more wastewater sludge is taken, the less P_2O_{5total} in the product, but the greater the relative content of the assimilable form of P_2O_5, the water-soluble form of CaO, organic substances and humic substances. As can be seen from the table 3 and 4 with the ratio of WWS: MM = 100: 10 and the norm of sulfuric acid 30% of stoichiometry produces an organomineral fertilizer containing $P_2O_{5total.}$ – 5.29 %; $P_2O_{5ass.}$by citric acid – 1.89 %, $P_2O_{5ass.}$: $P_2O_{5total.}$ – 35.68 %; $P_2O_{5water.}$: $P_2O_{5total.}$ – 3.98 %; $CaO_{total.}$ – 14.41 %; $CaO_{water.}$ – 1.43 %, $CaO_{water.}$: $CaO_{total.}$ – 9.94 %, organic matter – 42.92%; humic acids – 5.73%, fulvic acid -14.03%, water-soluble organic matter – 4.0%, SO_{3total} – 3,41%, SO_{3water}. – 1.11%, азот – 2.20%. With the same ratio of WWS to the mineralized mass, but with a norm of acid of 70%, a fertilizer containing $P_2O_{5total.}$ – 5.03 %; $P_2O_{5ass.}$by citric acid – 3.92 %; $P_2O_{5ass.}$: $P_2O_{5total.}$ – 77.98 %; P_2O_{5water}: $P_2O_{5total.}$ – 32.12 %; $CaO_{total.}$ – 13.69 %; $CaO_{water.}$ –5.96 %, $CaO_{water.}$: CaO_{total} – 43.51 %, organic matter – 40,80%; humic acids – 5.44%, fulvic acid – 13.33%, water-soluble organic matter– 3.80%, SO_{3total} – 7.31%, SO_{3water} – 2.02%, nitrogen – 2.09%.

At the request of agriculture, phosphorus fertilizer should have a high content of total and assimilable forms of P_2O_5, and the relative content of water-soluble forms of P_2O_5 should be at least 50%. Based on this requirement, the optimal norm of sulfuric acid for the decomposition of MM is 50% of stoichiometry, and the optimal ratio of WWS: MM can be considered 100: 30, at which the relative content of P2O5ass. is 52.71%.

In this organic fertilizer, using MM has the composition (weight. %): $P_2O_{5total.}$ – 6.77 %; $P_2O_{5ass.}$bylimitconc– 3.57%; P_2O_{5ass}: P_2O_{5total} – 52.71%; P_2O_{5water}: $P_2O_{5total.}$ – 18.14%; CaO_{total} – 19.97 %; CaO_{water} –6.43 %, CaO_{water}: $CaO_{total.}$ – 32.21%, organic matter – 27,28%; humic acids – 3,64%, fulvo acid -8.91%, water soluble organic matter – 2.54%, SO_{3total}. – 10.57%, SO_{3water}. – 3.51%, nitrogen – 1.40%. It should be noted that above approach to transfer P_2O_5 into acceptable form is promising technology in comparison with phosphoric processing low grade phosphorite by phosphoric acid [23-24].

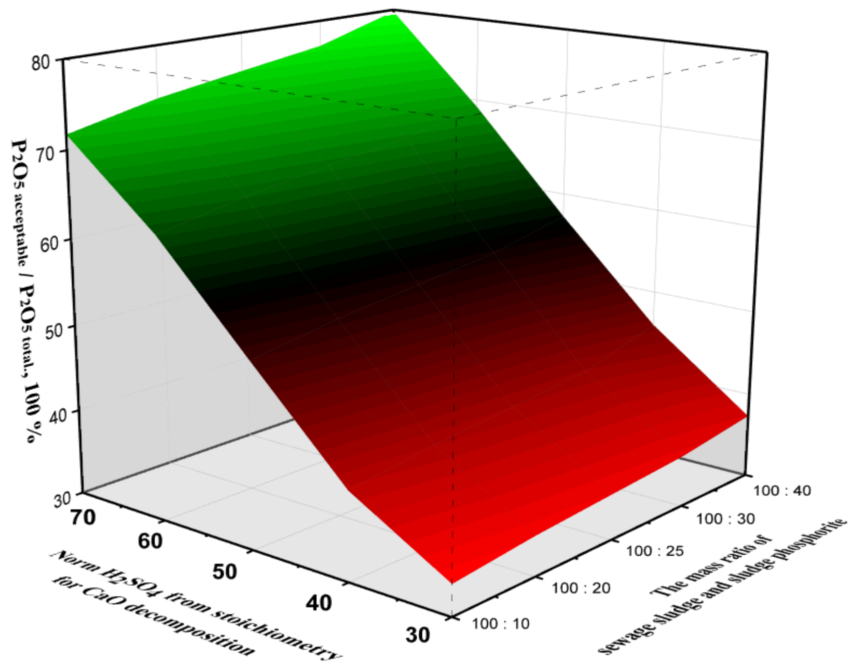

Fig. 1. The dependence of the change in the assimilable form of P_2O_5 by lim. to those from the norm of sulfuric acid and the mass ratio of WWS to MM

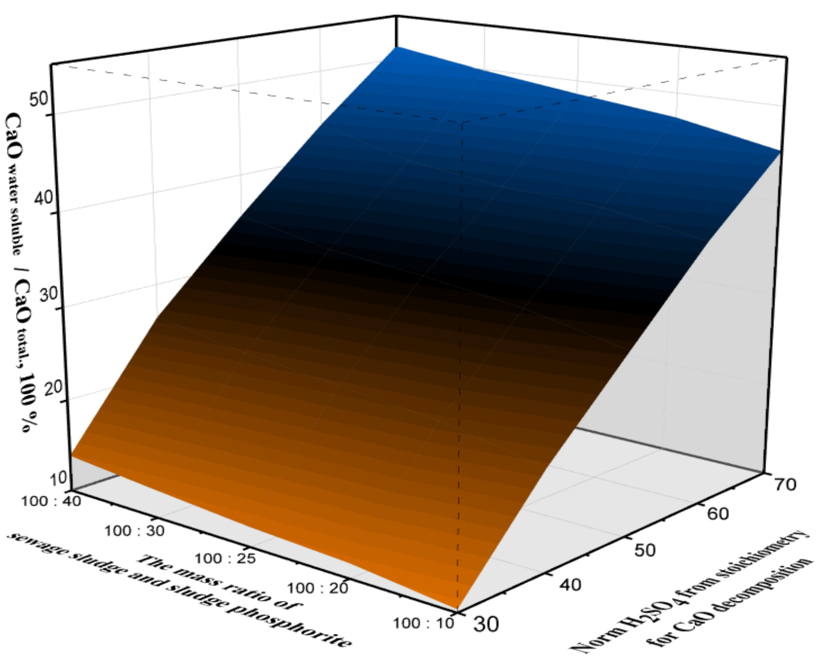

Fig. 2. Dependence of the change in the water-soluble form of CaO on the norm of sulfuric acid and the mass ratio of WWS to MM

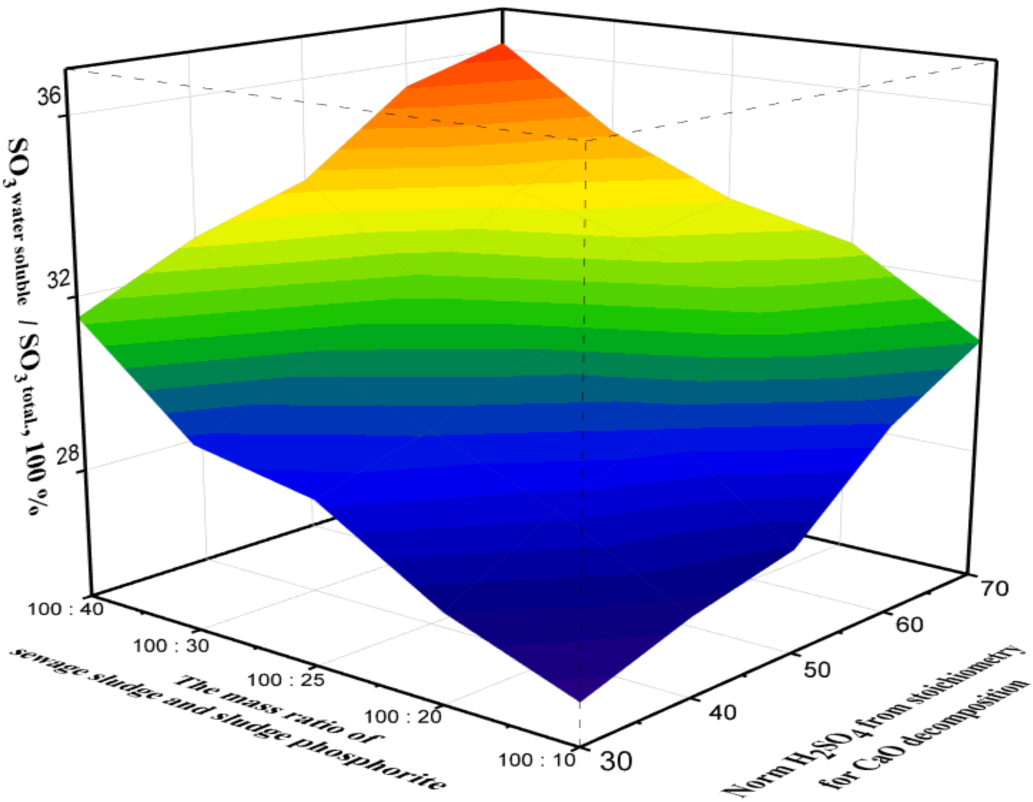

Fig. 3. Dependence of the change in the water-soluble form of SO_3 on the norm of sulfuric acid and the mass ratio of WWS to MM

4 Conclusion

Thus, the conducted studies convincingly show that, based on sewage sludge after dehydration or without it, using a small amount of sulfuric acid or other mineral acids used in the production of mineral fertilizers, it is possible to intensively process sewage sludge and sludge phosphorite into organomineral fertilizers

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