OBTAINING ORGANOMINERAL FERTILIZERS BASED ON INDUSTRIAL ACIDIFYING WASTEWATER AND GULIOB PHOSPHORITE

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Abstract
The work shows that organomineral fertilizers can be obtained by adding Guliob phosphorite (GPh) to municipal sewage sludge (SS), obtained on the basis of acidification in the presence of sulfuric acid in the pH range 2-4 with a mass ratio of SS : GPh = from 100 : 2 to 100 : 25. The kinetics of the transformation of indigestible forms of phosphorus and calcium into a plant-digestible form in poor hydrocarbons has been studied. It was shown that an increase in the mass fraction of phosphate raw materials in relation to acidified wastewater leads to an increase in the content of the total form of phosphorus pentoxide in composts, but to a decrease in the relative content of the digestible form of P2O5 and CaO. The longer the acidified waste water-phosphorite composts are kept, the more forms of phosphorus and calcium they can absorb for plants. When using this fertilizer in agriculture, the use of traditional scarce phosphorus fertilizers is greatly reduced.

Keywords: urban sewage sludge water (SS), Guliob phosphorite (GPh), sulfuric acid, phosphorus, calcium, humic acid, organomineral fertilizers.

Introduction

The rapid growth of the world's population from year to year and the sharp decline in arable land is exacerbating the global food problem. In this regard, one of the effective solutions to the food problem is the rational use of agrochemically effective mineral fertilizers to increase soil fertility, high and quality yields of agricultural crops. Therefore, it is important to obtain complex fertilizers that contain various nutrients necessary for plant development. This is due to the fact that in addition to macro-and micronutrients necessary for plants, complex fertilizers also contain humic substances that improve soil structure and fertility [1-3].
Among safe substances promising from the point of view of agro chemistry, compounds of natural origin, in particular, humic substances deserve special attention. Their formation (humification) is the second largest process of transformation of organic matter in the environment after photosynthesis, which involves a huge amount of carbon per year.

Humic substances are complex mixtures of biodegradation-resistant high-molecular dark-colored organic compounds of natural origin, formed during the decomposition of plant and animal residues under the action of microorganisms and abiotic environmental factors. Humic substances are a macro component of the organic matter of soil and water ecosystems, as well as solid fossil fuels.

Traditional sources of humic substances include peat, lignin, black cattle and poultry manure, as well as naturally oxidized coals and others.

It is known from the literature that peat bog plants, the main part of which consists of humus substances that increase soil structure and productivity, were formed during natural decay and natural decay in the presence of excess moisture. However, due to the lack of forests and wetlands in Uzbekistan, peat is almost non-existent [4].

However, due to the lack of forests and wetlands in Uzbekistan, peat is almost non-existent. Therefore, a wide range of technologies for the production of organic mineral fertilizers based on livestock, poultry waste and Kyzylkum phosphorites, oxidized Angren brown coal, ammophos, suprefos, urea and phosphogypsum waste from JSC "Ammophos-Maxam" has been developed [5, 6].

Other sources rich in humic substances can also include municipal sewage sludge (SS). The processes of obtaining organomineral fertilizers on the basis of SS were studied and it was found that the application of complex fertilizers to soils and crops not only increased their productivity, but also significantly reduced the cost of organomineral fertilizers obtained compared to other complex fertilizers [7, 8].

Raw materials for obtaining organic and organomineral fertilizers include: bedding manure, bedding-free manure, bird droppings, peat, brown coal, green manure, straw, sapropel, household and industrial waste, as well as SS [9].

In the patent [10], heavy metal ions are first removed from sewage sludge by treating urban sewage sludge (SS) with a solution of nitric acid with a concentration of 1.0-1.25 mol/dm^3 at a temperature of 50-70℃ for 10-20 minutes. The process is carried out at a ratio of solid and liquid phases equal to 1: 5. Under these conditions, the residual content of heavy metals corresponds to the standards for this type of fertilizer. After filtration, the residual acidity is neutralized with alkaline agents such as potassium hydroxide, ammonium hydroxide, calcium carbonate to obtain an organomineral fertilizer. The metals isolated from the sediment are precipitated in the solution and processed into sludge, from which they are then regenerated.

In next patent [11], 1000 l of a mixture is prepared from 200 l of SS water in a container which the mixture is circulated. The temperature of the prepared mixture is 40℃. Then, an alkaline reagent - 12.5 kg of NaOH is added to the container by the prepared mixture, and the mixture is alkalinity extracted with ultrasonic treatment for 60 minutes in an ultrasonic reactor. Also, the mixture is settled for a day to separate the ultrafine suspension of fibrous organic material, the liquid phase is drained and the insoluble part of the sediment is unloaded. As a result, 900 liters of liquid organomineral fertilizer are obtained and about 100 liters of the sediment of the latter are used as fertilizer for growing industrial and forest crops.

Materials and methods

However, in scientific studies based on SS, the microorganisms that cause pathogenic diseases in it are not completely deactivate. Therefore, in our opinion, it was considered expedient to obtain complex organomineral fertilizers based on inorganic additives containing SS, which are useful elements for plants. Termez city SS (wt.%) Moisture - 65.43; ash - 9.74; organic matter - 24.62; humic acids - 4.35; fulvic acids - 7.87; water-soluble organic substances - 4.23; P_2O_5 - 1.43; N 1.29; K_2O - 0.53; CaO - 4.31, sulfuric acid produced in Uzbekistan and phosphorite from the Guliob deposit in Sariosiyo district, Surkhandaryo region were selected. Table 1 shows the chemical compositions of Guliob phosphorite (GPh).

Table 1 **Chemical composition of Guliob phosphorite**

Content of components, wei. %							$P_2O_{5assi.}$ for trilon B $P_2O_{5tot.}$ %
P_2O_5	CaO	MgO	Al_2O_3	Fe_2O_3	F	CO_2	
7.88	20.64	1.02	0.62	0.45	1.36	8.03	21.32

Table 1 shows that GPh is characterized by a low content of phosphorus (7.88% P_2O_5), a high content of carbonates (20.64% CO_2) and a high value of the calcium module (CaO : P_2O_5 = 5.2).

Chemical analysis of the SS of the city of Termiz, GPh and products of their processing was carried out by the methods below. 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 on a water bath, drying the solid residue to a constant weight, followed by burning it to determine the ash content and subtract it. Humic acids were isolated by treating the products with a 0.1 n alkali solution, followed by acidification of the solution with mineral acid [12]. 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 a 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 forms of P_2O_5 were determined by the gravimetric method by precipitating the phosphate ion with a magnesia mixture in the form of magnesium ammonium phosphate, followed by calcining the precipitate at 1000-1050°C according to GOST 20851.2-75. Digestible forms of P_2O_5 were determined by solubility both in 2% citric acid and in 0.2 M Trilon B solution. CaO content was determined complexometrically : by titration with 0.05 N Trilon B solution in the presence of fluorexone indicator. 92% H_2SO_4 was used to acidify SS. The experiments were carried out as follows: first the measured sulfuric acid was poured into a glass reactor with a volume of 5 l, and then a certain amount of measured SS was gradually added to it. Sulfuric acid was acidified by adding SS : H_2SO_4 = 100:10 to 100:50 by weight relative to the organic component in SSW. In the last stage of the experiment, complex type organomineral fertilizers were obtained by adding to the acidified SS slurry: GPh = 100 : 10 to 100 : 50 by weight. The experiments were performed at 25°C temperature and for 60 min.

Results and Discussion

The results obtained are shown in Table 2.

It can be seen from them that $P_2O_{5tot.}$ as the weight ratio of GPh added to the acidified SS porridge increases. $P_2O_{5assi.}$ $CaO_{tot.}$ $CaO_{assi.}$ $CaO_{wat.}$ while the soluble forms were found to be increased, the organic content of SS as well as the humic content was found to be reduced. For example, SS organic : H_2SO_4 = $P_2O_{5tot.}$ in products with the addition of Guliob phosphorite in a ratio of 100 : 10 to 100 : 50 to the fermented SS porridge in the ratio of 100 : 10 by weight. $P_2O_{5assi.}$ $CaO_{tot.}$ $CaO_{assi.}$ $CaO_{wat.}$ forms from 3.94 to 5.33%, respectively; 1.95 and 2.12% respectively; 13.88 and 25, 78% respectively; 8.26 and 13.59% respectively; Organic content and humus content decreased from 44.53 to 24.60% and from 29.75 to 16.44%, respectively, while increasing from 1.72 to 4.29%. The best performance in this study was found in products with the addition of Guliob phosphorite in a ratio of 100 : 10 to 100 : 50 to the acidified SS slurry in the ratio of SS organic : H_2SO_4 = 100 : 50 by weight. Here $P_2O_{5tot.}$ $P_2O_{5assi.}$ $CaO_{tot.}$ $CaO_{assi.}$ $CaO_{wat.}$ forms from 3.15 to 4.80%, respectively; 2.82 and 3.78% respectively; 11.08 and 23.21% respectively; 10.84 and 18.99% respectively; Organic content and humus content decreased from 35.56 to 22.15% and from 23.76 to 14.80%, respectively, while increasing from 6.03 to 14.34%.

Table 2 **Composition of complex fertilizers based on SS sulfuric acid and GPh**

Weight ratio SS : GPh	$P_2O_{5tot.}$	$P_2O_{5assi.}$	$P_2O_{5wat.}$	$CaO_{tot.}$	$CaO_{assi.}$	CaO_{wat}	Organic	Humic
Weight ratio SS organic : H_2SO_4 = 100 : 10								
100 : 10	3,94	1,95	0,21	13,88	8,26	1,72	44,53	29,75
100 : 20	4,47	2,07	0,20	18,40	10,50	2,55	37,13	24,81
100 : 30	4,84	2,10	0,19	21,60	12,07	3,14	31,77	21,23
100 : 40	5,12	2,11	0,16	23,97	13,10	3,72	27,75	18,54
100 : 50	5,33	2,12	0,13	25,78	13,59	4,29	24,60	16,44
Weight ratio SS organic : H_2SO_4 = 100 : 20								
100 : 10	3,71	2,21	0,23	13,08	8,57	3,24	41,97	28,04
100 : 20	4,28	2,38	0,24	17,60	10,92	4,78	35,51	23,73
100 : 30	4,68	2,47	0,22	20,86	12,62	5,93	30,69	20,50
100 : 40	4,98	2,49	0,19	23,32	13,84	6,92	26,99	18,03
100 : 50	5,19	2,50	0,15	25,14	14,20	7,96	23,99	16,03
Weight ratio SS organic : H_2SO_4 = 100 : 30								
100 : 10	3,51	2,50	0,27	12,35	9,01	4,35	39,63	26,48
100 : 20	4,09	2,73	0,26	16,82	11,94	6,34	33,93	22,67
100 : 30	4,52	2,86	0,25	20,13	14,12	7,90	29,62	19,79
100 : 40	4,83	2,89	0,22	22,64	15,61	9,11	26,21	17,51
100 : 50	5,08	2,92	0,18	24,60	16,35	10,46	23,47	15,68
Weight ratio SS organic : H_2SO_4 = 100 : 40								
100 : 10	3,32	2,70	0,31	11,68	10,00	5,33	37,49	25,05
100 : 20	3,91	3,13	0,30	16,08	12,88	7,65	32,44	21,67
100 : 30	4,35	3,42	0,29	19,39	14,76	9,34	28,52	19,06
100 : 40	4,68	3,61	0,26	21,94	15,56	10,88	25,39	16,97
100 : 50	4,95	3,70	0,21	23,96	16,33	12,62	22,86	15,28
Weight ratio SS organic : H_2SO_4 = 100 : 50								
100 : 10	3,15	2,82	0,36	11,08	10,84	6,03	35,56	23,76
100 : 20	3,73	3,23	0,35	15,36	14,58	8,73	30,99	20,70
100 : 30	4,18	3,50	0,34	18,64	17,02	10,86	27,41	18,32
100 : 40	4,53	3,70	0,30	21,22	18,06	12,70	24,56	16,41
100 : 50	4,80	3,78	0,24	23,21	18,99	14,34	22,15	14,80

$P_2O_{5tot.}$ in the composition of phosphorus fertilizers used in agricultural crops. No matter how high the shape, the $P_2O_{5assi.}$ forms requires no less than 50%. In almost all organomineral fertilizers obtained by us, it was found that the $P_2O_{5assi.}$ form is not less than 50%.

Conclusions

It can be concluded from the results of scientific research that organomineral fertilizers can be obtained first by acidifying SS with sulfuric acid and then by adding Guliob phosphorite to the acidified SS slurry. It was found that the elements of phosphorus and calcium in plants containing Gph are absorbed by inorganic and organic acids.

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