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STUDY OF THE POSSIBILITIES OF UTILIZATION WASTES FROM PHOSPHORUS INDUSTRY IN MINERAL-ORGANIC FERTILIZERS

BADANIA NAD MOŻLIWOŚCIĄ WYKORZYSTANIA W NAWOZACH MINERALNO-ORGANICZNYCH ODPADÓW Z PRZEMYSŁU FOSFOROWEGO

Abstract: The possibilities of agricultural utilization of wastes from the phosphorous industry were presented. Wastes from the industrial plant producing phosphorous salts were chemically analyzed in order to determine chemical composition, and in the next step the agricultural tests allowing to estimate the toxicity of waste were carried out. The relatively optimal dose, which can be applied in the prescription of mineral-organic fertilizer without causing damages in cultivations, was determined.

Keywords: phosphogypsum, sodium fluorosilicate, after-neutralization slimes, mineral-organic fertilizers

The degradation of the environment, one of the most considerable problems in the World, occurs as a consequence of negative phenomenons, caused by the irrational economy as well as the lack of sufficient natural environment protection. New technologies are still in progress of developing consuming more raw materials, including the large amounts of water, resulting in higher amounts of sewages and wastes. It is possible to conclude the amount and composition of industrial wastes on the basis of the branch of industry profile. Omitting waste management creates serious environmental problems. In Poland an about 140 millions kg of industrial wastes are produced annually. Raw material deficiencies connected mainly with the progress observed in the East economic (India, China) should be a stimulus of rational utilization of sewages and wastes that are produced in different

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branches of industry enabling maximum utilization of valuable contents contained in them [1, 2].

Nowadays the principles of the Sustainable Development, which aim is reconciliation of economic, social and environmental aspects, include prescriptions concerning calculating the life cycle of the product from *cradle to grave*. This idea is connected with maximum utilization of raw materials. It prefers waste-free and integrated technologies, determining not only the way of manufacturing products but also utilization of wastes produced. On the basis of signed by Poland Agenda 21, different ecological programs which were formalized in standards regarding to environmental management have been developed [3–5].

Wastes from the phosphorous compounds industry contain a certain amounts of the essential nutrients for the plants, mainly phosphorus. Application in the agriculture, in particular in degraded lands rehabilitation, all of wastes, fit for this destination, is the extremely important problem from the economical and environmental point of view. In many cases this wastes can be used as a components in mineral-organic fertilizers. However, many experiments, for estimation of composition and usefulness of wastes, and studies of fertilizer composition for specific cultivations should be done. The selection and the amount of fertilizer elements is dependent on the species and demand of plant [6].

Materials and methods

The aim of research was determination of chemical composition of wastes from the phosphorus salts factory, applied as components during production of household detergents in domestic chemistry. The main product, manufactured at the factory, is the extraction phosphoric acid and sodium tripolyphosphate. In these processes the following wastes are produced:

– phosphogypsum, in the process of obtaining H_3PO_4 with extraction method,
– sodium fluorosilicate, in the process of defluorinating phosphoric acid,
– wastes from the sedimentation pond, where the sodium fluorosilicate and after-neutralization slimes are being stored,
– technological after-neutralization slimes from Varney filters,
– after-neutralization slimes from the press.

Chemically-agricultural assessment of wastes

The range of research included physicochemical analysis of wastes from the phosphorous industry. The following were determined:

– dry remains (waste from sedimentation pond) – in Sartorius apparatus – according to PN-78/C-04541,
– P_2O_5 content – using colorimetric method – with using of yellow phosphorous--vanadium-molybdenum complex and measurement of absorbance at wavelength λ = 420 nm, according to PN-ISO 5310:1994,

– calcium content [wt.% of CaO] – with using complexometric method with ethylenediaminetetraacetic acid, according to PN-R-64803/97,

– sulphates content [wt.% of SO_3] – with using scale method with production of the barium sulphate precipitate, according to PN-90/C-84089,

– silica and insoluble in hydrochloric acid parts content [wt.% of SiO_2 + insoluble parts] – using scale method with emission of SiO_2, according to PN-90/C--84089,

– fluorine content – with using method with ion selective electrode with apparatus from the Orion company,

– iron and aluminium oxides content [wt.% of R_2O_3] – the estimation consists in precipitation of iron and aluminium with ammonia in the form of hydroxides, calcination of the precipitate to oxides and subsequently scale analysis, according to BN-86/6710-03/25.

The agricultural tests were carried out according to the standard PN-94/R-65950. These examinations have been consisted in estimation of the germination ability of the garden cress (*Lepidium sativum*) seed on medium from the soil with the addition of wastes. The aim of the biological test was the checking that the wastes were not limiting germination and growth of the cress, what means that the wastes were not toxic for the plants. The aim of introduced researches was also preliminary estimation of the optimal dose of waste which can be applied in the prescription of mineral-organic fertilizer. Tests were carried out in three series, on Petri dishes. The medium heavy soil free of germination limiting factors was the substrate. The substrate was thoroughly mixed with the wastes in the amount specified below and wetted with redistilled water. The seeds were distributed on the substrate so that they were not in contact with each other and did not stick to the edge of the dish. The germination capacity was evaluated after 10 days.

Series 1: The waste and the soil at a mass ratio of	1 : 3	– 25 of seeds
	1 : 4	– 25 of seeds
	1 : 5	– 25 of seeds
Series 2: The waste and the soil at a mass ratio of	1 : 10	– 50 of seeds
	1 : 15	– 50 of seeds
	1 : 20	– 50 of seeds
Series 3: The waste and the soil at a mass ratio of	1 : 50	– 50 of seeds
	1 : 100	– 50 of seeds
	1 : 200	– 50 of seeds

Results and discussion

Results of physicochemical analyses of tested wastes are presented in Table 1. Examinations showed that wastes contain plant nutrients. In further research sodium fluosilicate has not been taken into consideration, due to its toxic activity.

Table 1

Chemical composition of wastes from phosphorus compounds production plants

Analysed compound	Phospho-gypsum	Sodium fluosilicate	After-neutraliza-tion slimes from Varney filters	After-neutraliza-tion slimes from the press	Wastes from the sedimentation pond
	mass %				
P_2O_5	2.26	7.46	19.98	23.03	11.87
CaO	25.01	1.47	4.84	9.12	8.53
SO_3	42.95	0.72	0.86	0.79	0.22
SiO_2+insoluble parts	1.42	2.70	1.86	4.77	2.40
Fe_2O_3+Al_2O_3	2.16	50.49	0.58	0.76	0.29
F	0.37	7.05	3.91	3.50	4.75

Agricultural tests for germination is shown in the Table 2.

Table 2

Results of *Lepidium sativum* germination test

Mass ratio of waste and soil		Germination capacity [%] of normally germinating seeds			
		phosphogypsum	after-neutralization slime from Varney filters	after-neutralization slime from press	waste from sedimentation ponds
Series I	1 : 3	100.0	—	—	—
	1 : 4	100.0	—	—	—
	1 : 5	100.0	—	4.0	—
Series II	1 : 10	93.5	2.2	28.3	15.2
	1 : 15	97.9	12.5	41.5	72.9
	1 : 20	97.9	25.0	70.8	80.0
Series III	1 : 50	98.2	74.5	93.6	93.8
	1 : 100	98.8	89.4	93.6	95.9
	1 : 200	100.0	98.4	97.9	98.0

In Table 2 the results of germination cress (*Lepidium sativum*) seeds test, on the different wastes, were presented. It was observed that overdose of waste caused total or partial development of plant impossible. In case of phosphogypsum the determination of optimal dose was very difficult, because large amount of insoluble calcium sulphate caused that this waste did not have influence on the inhibition of germination. In the case of the rest of the wastes it was observed that with the decreasing dose of waste, introduced into the soil, the amount and the quality of plant were increased. Dishes with the cress seeds on the soil without waste serve as a comparison sample.

Biological tests for estimating the toxicity of waste were carried out on phospho-gypsum, sodium fluosilicate, slimes and waste from the sedimentation pond. It was observed that the ability of the seed germination of the cress was different on all objects. Comparison of different kind of doses of these wastes in order to determine the

optimal dose was one of purposes. During applying the proportion of waste to the soil, 1:3, 1:4 and 1:5 it was possible to observe germination only on the Petri disches with phosphogypsum. Simultaneously with the decrease of waste doses better ability to germinate was observed in all objects. When weight ratio of the waste to soil was 1:200 the efficiency of germination reach satisfying level, near to the 100 %.

Nutrient requirements of chosen plants

Nutrient requirements of plants fulfill the amount of element, which should be taken by plant to yield optimum crop. This value is expressed in kg of compound per 1 hectare. For guarantee plant proper amount of nutrients, in whole growing season, it is necessary to conduct an efficient fertilization, which condition is knowledge of nutrient requirements of a particular species of plants [7–11].

Compositions of mineral-organic fertilizers for corn and winter rye were proposed on the basis of the experimental results and literature data. As an addition to mineral--organic fertilizers the lignite and the peat were used. The possibilities of utilization the lignite as a fertilization are great, because in Poland the deposits of lignite are not exploited for energetic purposes (for the reason of oversalinity). Using lignite and peat plays a crucial role in terms of introduction of large amount of organic matter into fertilization, which has a lot of benefits on physical, chemical and biological processes.

Table 3

The components content in mineral-organic fertilizer [kg/Mg of fertilizer] for corn, based on the wastes from sedimentation ponds and lignite (dose of fertilizer: 0.3 Mg/ha)

No.	Component	Pure compound content [kg] in 1 Mg of fertilizer	Amount of introduced components with waste from sedimentation pond [kg]	Amount of introduced components [kg/ha]	Amount of introduced components [kg]
1	N	24.8		70.8	244.9 NH_4NO_3
2	P_2O_5	8.0	8.0		
3	K_2O	39.2		72.49	250.7 K_2SO_4
4	CaO	9.6	5.7	3.9	13.5 CaO
5	MgO	3.2		9.55	33.0 $MgSO_4$
6	B	0.104		0.59	2.04 H_3BO_3
7	Cu	0.104		0.41	1.42 $CuSO_4 \cdot 5H_2O$
8	Mn	0.64		2.60	8.99 $MnSO_4 \cdot 4H_2O$
9	Mo	0.012		0.03	0.10 $Na_2MoO_4 \cdot H_2O$
10	Zn	0.8		3.52	12.18 $ZnSO_4 \cdot 7H_20$
11	Lignite			57.8	200.0
12	Waste			67	231.7
Altogether				252.1	~1000

In Table 3 the components content in mineral-organic fertilizer for corn, based on the wastes from sedimentation ponds and lignite, was presented. The amount of wastes, which are introduced with fertilizers per hectar of field, was 67 kg. This amount covers demand of corn for phosphorus and partially for calcium. In the last two columns an amount of introduced components in kg per hectare and in 1 Mg of fertilizers was presented.

In Table 4 the components content in mineral-organic fertilizer for winter rye, based on the wastes from after-neutralization slime from the press and peat, was presented. The amount of wastes, which are introduced with fertilizers per hectar of field, was 260 kg. This amount covers demand of winter rye for phosphorus and partial for calcium. In the last two columns an amount of introduced components in kg per hectare and in 1 Mg of fertilizers was presented.

Table 4

The components content in mineral-organic fertilizer [kg/Mg of fertilizer] for winter rye based on the wastes from after-neutralization slime from the press and peat (dose of fertilizer: 1.8 Mg/ha)

No.	Component	Pure compound content [kg] in 1 Mg of fertilizer	Amount of introduced components with waste from sedimentation pond [kg]	Amount of introduced components [kg/ha]	Amount of introduced components [kg]
1	N	156		445.7	247.1 NH_4NO_3
2	P_2O_5	60	60		
3	K_2O	153		282.9	156.8 K_2SO_4
4	CaO	150	23.7	126.3	70.0 CaO
5	MgO	27		80.60	44.68 $MgSO_4$
6	B	0.33		1.86	1.03 H_3BO_3
7	Cu	0.142		0.56	0.31 $CuSO_4 \cdot 5H_2O$
8	Mn	0.998		4.04	2.24 $MnSO_4 \cdot 4H_2O$
9	Mo	0.021		0.052	0.029 $Na_2MoO_4 \cdot H_2O$
10	Zn	0.384		1.668	0.925 $ZnSO_4 \cdot 7H_20$
11	Peat			600	332.6
12	Waste			260	144.1
Altogether				1803.7	~1000

In the Figure 1 the percentage composition of a mineral-organic fertilizer for winter rye, based on the after-neutralization slimes from Varney filters and lignite, is shown. The amount of wastes, which are introduced with fertilizers per hectar of field, was 500 kg. This amount covers demand of rye for phosphorus and partial for calcium. The proposed fertilization is up to 1.8 Mg/ha.

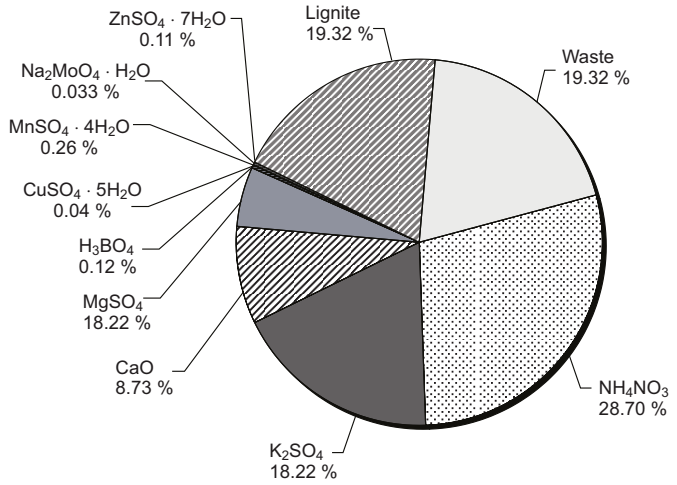

Fig. 1. Percentage composition of a mineral-organic fertilizer for winter rye, based on the after-neutralization slimes from Varney filters and lignite. The proposed fertilization: up to 1.8 Mg/ha

Conclusions

The aim of research was determination of chemical composition of wastes from the phosphorus salts factory. The phosphogypsum, sodium fluorosilicate, after-neutralization slimes from the filters and the press and wastes from sedimentation pond were analysed. Following the current trends and environmental protection regulations, recycling seems to be the best solution for wastes from phosphorus compounds production plants. The utilization of wastes in agriculture appear to be the most promising solution.

The satisfactory germination ability of cress (*Lepidium sativum*) seeds on all nine doses of phosphogypsum confirms the fact that a little amount of compounds from it penetrates into the soil. This amount has significant meaning for plant germination. Considering relatively large content of phosphorus in phosphogypsum satisfactory results were obtained.

The comparison of the results of the chemical analysis shows which waste can be used in fertilizationand which doses should be use. The main nutrients, which are in wastes, are phosphorus and calcium.

In spite of phosphorus and calcium content in phosphogypsum, this waste is not suitable for utilization in fertilizers. It contain relatively large amount of heavy metals, huge amount of sulphates, which precipitate calcium in insoluble calcium sulphate, and for that reasons its fertilizers worth is small. However, phosphogypsum can be used to land rehabilitation and for improving soil acidity.

The sodium fluorosilicate is contaminated by phosphorus compounds and by calcium sulphate, which co-precipitate with phosphorus during production of sodium tripoly-polyphosphate. This kind of waste is not suitable for agricultural utilization, because of huge fluorine content.

The after-neutralization slimes is a mixture of soluble sodium phosphates, insoluble phosphates of calcium, aluminium and iron. This kind of wastes can be used to the fertilization purposes.

The greatest abilities of utilization as a component of mineral-organic fertilizers slimes have after-neutralization slimes from Varney filters and from the press, as well as wastes from the sedimentation pond where after-neutralization slimes from the sodium tripolyphosphate production are being stored. In the composition of that wastes the significant amount of phosphates and calcium – that can be used as nutrients – was visible.

The mineral-organic preparations, which are proposed to use, can be independent substratum in chosen plant species (corn and winter rape). In this aim the suitable amounts of waste, inorganic components and lignite and peat (as an organic component) were used.

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BADANIA NAD MOŻLIWOŚCIĄ WYKORZYSTANIA W NAWOZACH MINERALNO-ORGANICZNYCH ODPADÓW Z PRZEMYSŁU FOSFOROWEGO

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Abstrakt: Przedstawiono możliwości rolniczego wykorzystania odpadów z przemysłu fosforowego. Odpady z zakładu produkującego sole fosforowe poddano analizie chemicznej w celu zbadania składu chemicznego, a następnie przeprowadzono testy rolnicze pozwalające ocenić toksyczność odpadów i ustalić optymalną dawkę, jaką można wykorzystać w recepturze nawozu mineralno-organicznego bez spowodowania szkód w uprawach.

Słowa kluczowe: fosfogips, fluorokrzemian sodowy, szlamy poneutralizacyjne, nawozy mineralno-organiczne