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ORIGINAL PAPER

Obtaining of Suspension Fertilizers from Incinerated Sewage Sludge Ashes (ISSA) by a Method of Solubilization of Phosphorus Compounds by *Bacillus megaterium* Bacteria

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Abstract The article presents research results on obtaining phosphorus suspension fertilizers on the basis of microbiologically activated sewage sludge ashes and Morocco phosphate rock. The fertilizers were manufactured with the use of a laboratory reactor, as well as an experimental pilot plant for liquid fertilizers production and then subjected to physicochemical properties tests that have allowed to asses the quality of the obtained products and to appoint new directions for further research on obtaining phosphorus suspension fertilizers on the basis of microbiologically activated renewable resources of phosphorus. The tests have confirmed that it is possible to produce phosphate fertilizer suspension by using the *Bacillus megaterium* for solubilization of phosphorus, and that the process is not complicated. However, obtained fertilizers are characterized by low P_2O_5 content.

Keywords Microbiological solubilization · Renewable phosphorus resources · Incinerated sewage sludge ashes · Suspension fertilizers · Phosphorous fertilizers

Introduction

Nowadays, more consumers are searching for products having functional properties, containing nutrients coming from natural resources, but not being chemical synthesis products [1]. Phosphate rocks, which are non renewable raw materials, are the basic raw materials used in phosphorus fertilizers production. From the environmental point of view, we are dealing with phosphorus uptake from an ore (phosphate rocks, apatites) and its effective dispersion in the environment as a result of the farming [2]. There is no phosphorus substitute, but at the same time, phosphorus after the 'use' does not disappear and it can be subjected to recycling. Simultaneously, the growing demand for phosphorus fertilizers is observed (Table 1) [3]. Thus, the attemps to obtain phosphorus from the renewable resources such as different waste materials, i.e. bone wastes, fish bone, and ashes from biomass incineration from sewage treatment plants [4], have become very essential.

The application of fertilizers from sewage sludge ashes to agricultural land is generally considered to be the good way to recycling phosphorus because the sewage sludge ashes (SSA) have usually high content of P_2O_5. However, the SSA are not ideal source of phosphorus because they often contain significant amounts of undesirable metals and phosphorus compounds and they must be converted into available form [5, 6]. Previous studies of phosphorus recovery from SSA have looked at acid or base leaching. According to these studies, the acid leaching is more effective than base leaching [7, 8]. But still the use of sulfuric acid for phosphorus extraction is not always commercially reasonable. Because of this, it is interesting idea to conduct bioleaching process using microorganisms that produce organic or mineral acids [9, 10], especially taking into account the further course of solubilization in the soil after the application of fertilizer containing microorganisms [11].

One of the possibility is the use of a natural ability of some microorganisms (bacteria and fungi) for solubilization of phosphates [2]. The effectiveness of activation

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Table 1 The world's fertilizers demand in the years of 2012–2016 (thousands tones of the component) [3]

Year	2012	2013	2014	2015	2016
N	109,928	111,558	113,063	114,504	115,956
P_2O_5	41,525	42,731	43,487	44,251	45,013
K_2O	28,626	29,494	30,879	32,208	33,163

(solubilization) processes of phosphorus from mineral resources and different types of wastes, depends on numerous essential factors, i.e. the type of phosphorus raw material subjected to solubilization, types of the microorganisms, inorganic additives, as well as a method of preparing the products and conducting the process. Bacteria (Phosphorus Solubilizing Bacteria-PSB) and fungi (Phosphorus Solubilizing Fungi—PSF) can be used for the process. In total, both of the microorganism groups that activate phosphorus are defined by the term Phosphate Solubilizing Organizm- PSO [12, 13]. Two groups of processes are realized in practice:

composting of organic waste with an optional addition of phosphorus raw materials (activation of phosphorus contained in raw materials takes place during the composting processes) [14],

activation of phosphorus compounds contained in high quality raw materials and in waste raw materials using microorganisms (fungi and bacteria) and optionally elementary sulphur [2].

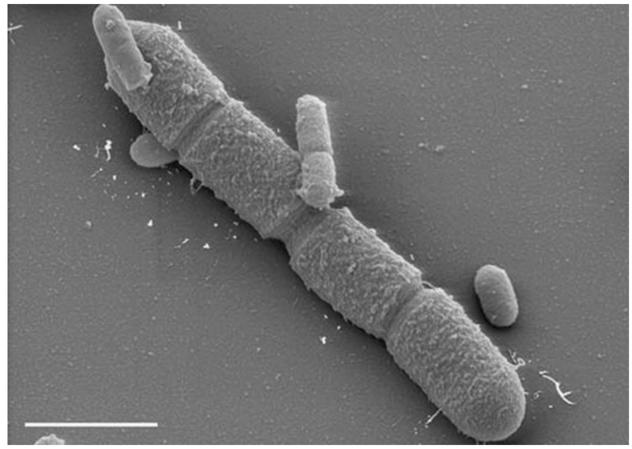


Fig. 1 *B. megaterium*, next to *E. coli* cell. The *B. megaterium* cell volume is 100 times bigger. The *white line* marks the length of 2 μm [18]

Bacillus megaterium and *Acidithiobacillus ferrooxidans* [15, 16] bacteria or *Aspergillus niger* [17] fungi are examples of bacteria that allow the microbiological solubilization process to happen. *Bacillus megaterium*, which were used in this study, produce the mixture of citric acid, lactic acid and propionic acid which react with phosphorus compounds from SSA and convert them to available form [2, 9, 10, 15] (Fig. 1).

The aim of the study was to manufacture of suspension fertilizers on the basis of phosphorus waste materials (ash and phosphate rock as controls) and *B. megaterium* for the field experiments conducted by University of Warmia and Mazury in Olsztyn.

Table 2 Content of particular compounds in SSA and Morocco phosphate rock

Compound	Unit	Content	
		Ash	Phosphate rock
Total P_2O_5	wt%	24.7	32.4
Neutral ammonium citrate-soluble P_2O_5		7.2	1.3
Water-soluble P_2O_5		Below the determination limit	0.5
CaO		18.0	51.9
K_2O		1.9	0.08
Al_2O_3		9.7	0.35
Fe_2O_3		6.5	0.22
MgO		3.8	0.32
Na_2O		0.57	1.11
SiO_2		33.2	1.71
As	mg/kg	4.1	1.43
Ni		64	28.9
Cd		1.23	15.8
Pb		40	6.2
Hg		0.030	0.018

The contents of heavy metals in SSA was lower than the limits of Polish fertilizer standards

Table 3 The content of culture medium for *Bacillus megaterium* multiplication

Compound	Amount (g/dm^3)
Glucose	100
Ammonia sulphate (VI)	5
Sodium chloride	2
Heptahydrate magnesium sulphate (VI)	1
Potassium chloride	2
Monohydrate manganese sulphate (VI)	0.02
Heptahydrate iron sulphate (VI)	0.02
Yeast extract	5
Phosphate compound	30

Methodology

The Description of Raw Materials

Ashes coming from incineration of sewage sludge from Łyna sewage–treatment plant near Olsztyn were used as a phosphorus raw material. A suspension fertilizer obtained on the basis of Morocco phosphate rock was the control. The content of particular compounds in raw materials has been presented in Table 2.

Bacillus megaterium bacteria was delivered by Wroclaw University of Technology and their multiplication was conducted on a culture medium having the content described in Table 3.

Measurement Methods

Determination of total phosphates was conducted by a gravimetric method with the use of quinoline phosphomolybdate according to EC Regulation No 2003/2003.

Determination of assimilable phosphates, soluble in 2 % citric acid was also conducted by a quinoline-molybdate gravimetric method. The determinations were proceeded by an extraction conducted with 2 % citric acid. The extraction was proceeded according to EC Regulation No 2003/2003.

A water soluble phosphate was determined by a phosphomolybdate blue spectrophotometric method with the use of a Jenway 6300 spectrophotometer.

The pH measurement of the reaction mixture was conducted with the use of an Elmetron CX-501 multifunctional pH meter.

A sedimentation tests of the suspensions were conducted in the way that the fertilizer sample was placed in a transparent air-tight 1 dm^3 bottle and the content was shaked to mix it well. Subsequently, the bottle was left until the mixture deposition started and then changes after 24 h were observed. Ash powdered to below 200 and 50 μm was used in the research. For each of the ashes, 3 samples of 7.5; 10 and 12.5 wt% of bentonite, were prepared.

Methods and Principles of the Conducted Processes

The laboratory tests of obtained suspension phosphate fertilizers were conducted on the IKA LR-2. ST Package 1 chemical reactor with a working volume of 2 dm^3 equipped with a EUROSTAR stirrer. The reactor measured and registered the following parameters: temperature, number of rotations, torque.

Preparing a culture medium for the *B. megaterium* bacteria was the first stage of suspension fertilizer production. The trials were conducted with the concentration of phosphate raw material in mixture of $c = 30$ g/1 dm^3. The particular components of the culture medium were introduced to proper amount of water—1.5 dm^3. Afterwards, the obtained solution was brought to the boil (100 °C) in order to sterilize

Fig. 2 The experimental pilot plant for liquid fertilizer production

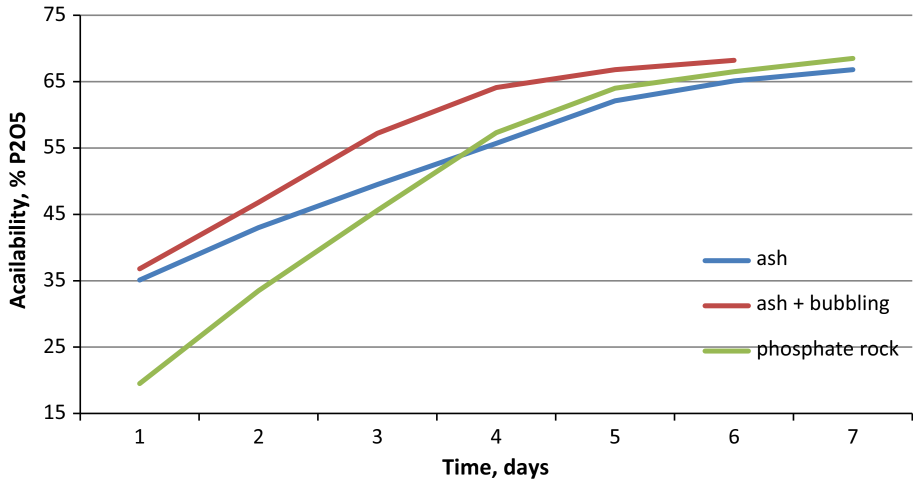


Fig. 3 Changes in ammonium citrate-soluble P_2O_5 content in relation to total P_2O_5 during the process of suspension fertilizers production on the basis of *Bacillus megaterium* bacteria

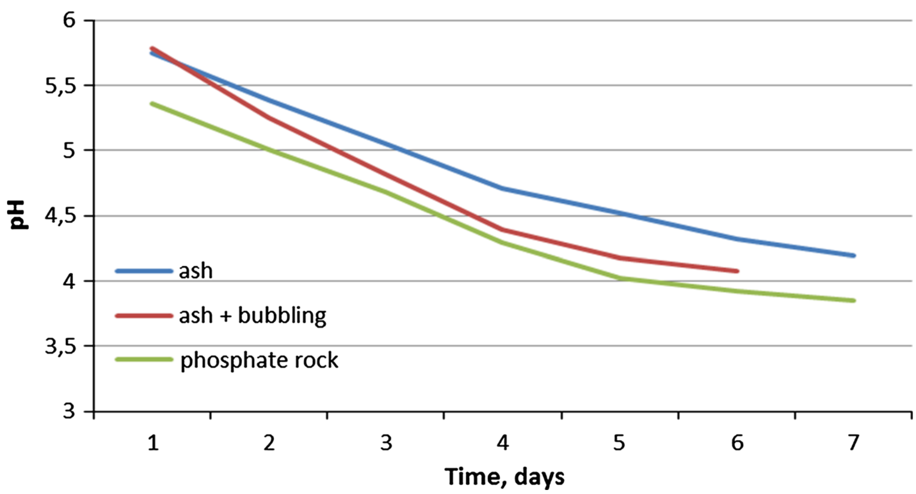


Fig. 4 Changes in pH value during the process of conducting the suspension fertilizer on the basis of *Bacillus megaterium* bacteria

Table 4 P_2O_5 contents of particular forms in fertilizer products

P_2O_5 form	Type of product depending on the raw material used		
	Ash	Ash + bubbling	Phosphate rock
Total P_2O_5	0.804	0.811	1.02
Neutral ammonium citrate-soluble P_2O_5	0.531	0.540	0.673
Water-soluble P_2O_5	0.501	0.498	0.585

it. After conducting this process, the solution was left for cooling down to temperature of about 35 °C. After the cooling, the batch was inoculated by a bacteria solution in an amount equalling about 10 % of the reactor batch. The prepared bacterial culture was grown in the temperature of 35 °C for 7 days and in the case of laboratory tests with additional aeration—for 6 days and the numbers of rotations were 60 rpm and torque was 140 Ncm. During the process, on every 24 h, an additional portion of the cultural medium, was introduced. The introduced additional culture medium equalled 10 % of the reactor batch mass during the whole process. At the end of the process bentonite was added for the stabilization of suspension. Bentonite was added to reach a pH of 7 or, if it's necessary, until stable suspension was obtained.

Tests were also carried out at pilot scale. The pilot scale tests were conducted in a reactor having operating volume of 100 dm^3 (Fig. 2). The reactor was equipped with a mechanical mixer and electric heating. The procedure for testing was the same as in the case of laboratory tests. Pilot scale tests have not been conducted with additional aeration of the reaction mixture.

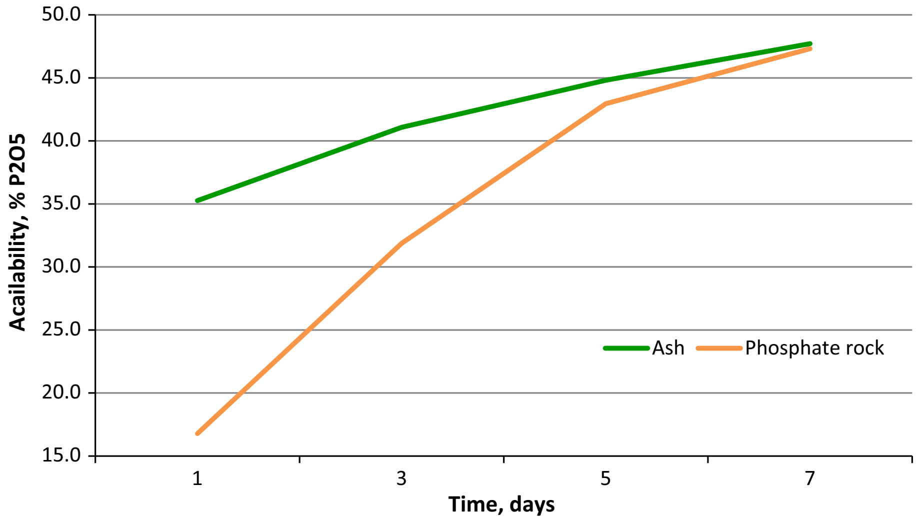


Fig. 5 Changes in in ammonium citrate-soluble P_2O_5 content in relation to total P_2O_5 content in suspension fertilizers using *Bacillus megaterium* bacteria

Table 5 Particular forms of P_2O_5 contents in obtained products, %mass

P_2O_5 form	Type of product depending on the raw material used	
	Ash	Phosphate rock
Total P_2O_5	2.411	2.98
neutral ammonium citrate-soluble P_2O_5	1.15	1.41
water-soluble P_2O_5	0.801	1.05

Research Results

The research on production process of suspension fertilizers on the basis of *B. megaterium* bacteria began from conducting laboratory scale tests, aiming at determining the initial process parameters for further pilot scale research.

Laboratory Tests

According to conducted laboratory research, it is stated that *B. megaterium* bacteria could be used to obtain phosphorus fertilizer at which about 2/3 of P_2O_5 is in the form of available to plants. Moreover, it was observed that additional airing of mixture, accelerates the gaining of optimal phosphorus compounds conversion rate to plant available forms but not influence its end value.

Figure 3 shows the changes in ammonium citrate-soluble P_2O_5 content in relation to total P_2O_5 during the process of suspension fertilizers production on the basis of *B. megaterium* bacteria. Figure 4 presents changes in pH value in reaction solution during the laboratory trials of obtaining the suspension fertilizers.

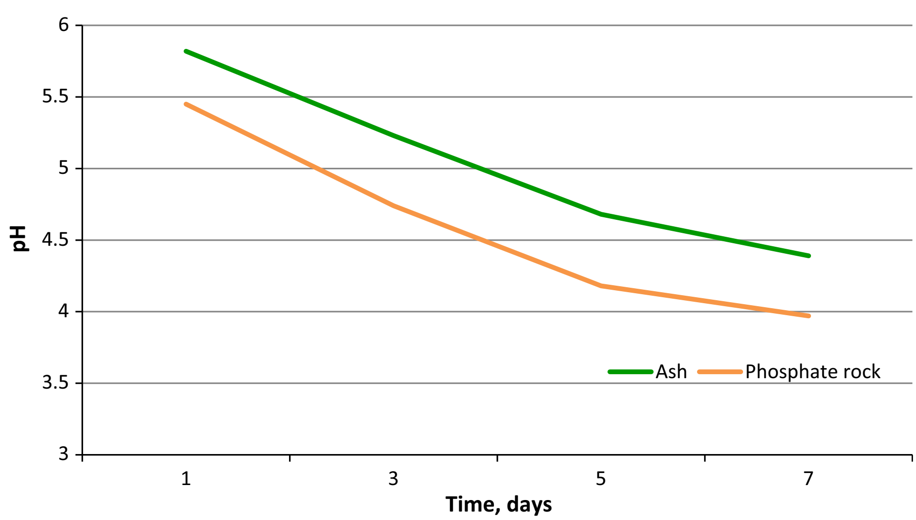


Fig. 6 Changes in pH value during the process of conducting the suspension fertilizer on the basis of *Bacillus megaterium* bacteria

Fig. 7 Images ilustrating delamination of fertilizer suspension based on ashes

Table 6 Volume of suspension after 24 h

Particle size of ash, μm	Below 200			Below 50		
Content of bentonite, %mass	7.5	10.0	12.5	7.5	10.0	12.5
Volume of suspension, cm^3	390	520	810	460	580	830

The initial dynamics of the increase of ammonium citrate-soluble P_2O_5 content is higher in fertilizer on the basis of phosphate rock than in the case of fertilizer on the basis of ash, however in both cases the end content of ammonium citrate-soluble P_2O_5 is similar.

In both cases changes in dynamics of pH values are similar. At the whole process for the fertilizer on the basis of phosphate rock, the lowest pH value is observed. Table 4 shows the final phosphorus contents at particular samples.

Pilot Plant Research

Pilot plant research has confirmed the results obtained on the basis of laboratory research, however in the case of pilot plant scale, the slightly decrease of dynamics of microbiological solubilization process was observed. Moreover, at the ½ technical scale research, the trials were conducted with the highest quantity of phosphate raw material and the concentration of mixture was c = 100 g/1 dm^3.

Figure 5 shows changes in ammonium citrate-soluble P_2O_5 content in relation to total P_2O_5 content during process of preparing the suspension fertilizers using *B. megaterium* bacteria.

The final content of available phosphorus forms is about 47 %, both in case of an ash fertilizer, as well as a phosphate one. A faster increase of soluble P_2O_5 in ammonia citrate can be observed for phosphate fertilizers, in the first 5 days of the process.

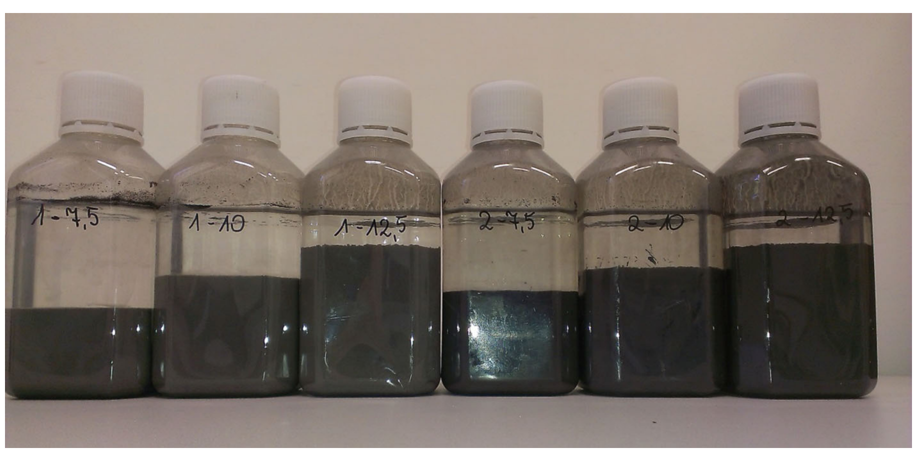
The pH value is lower during the preparation of phosphate-based fertilizer, but the changes of pH value are similar for both preparation processes of suspension fertilizers. Table 5 shows final contents of phosphorus forms in particular trials (Fig. 6).

The pilot plant research has showed that the increased supply of phosphate raw material does have limited impact on contents of available phosphorus forms at conducted trials with mixtures containing more phosphate raw material. Only total P_2O_5 content was increased in proportion to the total P_2O_5 content from laboratory trials with smallest quantity of phosphate raw material.

In comparison to studies on solubilization by microbs [9, 10] the content of available P_2O_5 in the obtained suspension fertilizers is about 10 times greater. However, recovery of P_2O_5 in this tests was lower than in the previously mentioned studies [7, 8] of the extraction of phosphorus from the ash by mineral acids. Comparing to these results was difficult due to various kinds of obtained fertilizers. Most of the research results concern a clear liquid fertilizers while our study has been conducted to obtained suspension fertilizers.

Figure 7 illustrates the problem of maintaining stability of the obtained suspension fertilizers. Sedimentation tests

Fig. 8 Images ilustrating the level of suspension delamination depending on the level of ash crushing and the content of bentonite



of the suspensions showed that after approx. 2 h of obtaining the fertilizer all solids particles settle onto the bottom of the bottle. In order to identify the cause of suspension delamination, the experiment was conducted in which the influence of the ash fineness and the amount of added bentonite on sedimentation was determined. From this experiment (Table 6) we concluded that the reduction of ash particles had a positive effect on the stability of the suspension. However, the key factor which most strongly influences the stability of the fertilizer was the amount of stabilizing agent. We observed the greatest stability of the suspension with the addition of bentonite at the 12.5 % by weight (Fig. 8).

Conclusion

The pilot plant tests have confirmed that it is possible to produce phosphate fertilizer suspension of the waste materials, using the *B. megaterium* for solubilization of phosphorus, and that the process is not complicated. However, obtained fertilizers are characterized by low P_2O_5 content and even the increase of quantity of phosphate raw material does not benefit on contents of available P_2O_5 forms.

The studies revealed a problem of low stability of the obtained suspension. In order to reduce delamination, additional gridding of raw phosphoric material is needed and the addition of a sufficiently large amount of bentonite.

Compared to traditional suspension fertilizers, the potential advantage of those types of fertilizers is the content of *B. megaterium* bacteria which introduced to soil could activate the accumulated phosphorus compounds.

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