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Suspension fertilizers based on alternative raw materials – the key to sustainability and closed nutrient cycles

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Abstract: The rapid, high increase in production costs and prices of mineral fertilizers leads to a reduction in their use by farmers, while fertilizer manufacturers consider the use of alternative raw materials and reducing the energy consumption of fertilizer production processes. Given these circumstances, special attention is warranted for suspension fertilizers. The manufacturing of suspension fertilizers is simplified and less energy intensive in comparison with solid fertilizers. This is achieved by omitting certain production stages such as granulation, drying, sifting, which usually contribute to more than half of the production costs. This paper presents the production procedure of suspension fertilizers tailored for cabbage cultivation, utilizing alternative raw materials such as sewage sludge ash and poultry litter ash. The final products are thoroughly characterized. The obtained fertilizers were rich in main nutrients (ranging from 23.38% to 30.60% NPK) as along with secondary nutrients and micronutrients. Moreover, they adhere to the stipulated standards concerning heavy metal content as outlined in the European Fertilizer Regulation. A distribution analysis has showed that suspension fertilizers contain nutrients in both liquid and solid phases. This arrangement facilitates their easy availability for plants and subsequent release upon dissolution in soil conditions. To assess process consistency, the production of the most promising fertilizer was upscaled. A preliminary technological and economic analysis was also conducted. The method of producing suspension fertilizers using alternative raw materials is a simple waste management solution offering nutrient recycling with the principles of circular economy. This approach not only encourages nutrient recycling but also curtails reliance on imported raw materials.

Introduction

The increasing demand for food results in the need to produce more and more fertilizers to promote the proper growth, development and weight gain of plants. However, the demand for fertilizers is not only in the food industry but also in the branch related to biofuel production (Rene et al. 2020). Two distinct trends in the application of fertilizers have been observed over the last decade. Developed countries are reducing their use of fertilizers by implementing the principle of fertilization appropriate to the needs of specific groups of plants. In countries with high population growth, the use of fertilizers will continue to increase due to food and feed production. The demand for solid fertilizers will remain high for logistical reasons. However, currently, liquid and suspension fertilizers are gaining more and more recognition due to their high nutrient concentration and the possibility of simultaneous irrigation of crops. This is particularly important in the current period of climate change and shifting the vegetation zones (Zalewski and Piwowar 2018, Bogusz 2022a).

Suspension fertilizers may contain primary nutrients: N, P, K, and secondary nutrients: Ca, S, Mg, Na, as well as micronutrients: Cu, Mn, Fe, Zn, B, Co, Mo in forms that dissolve in water, but also ingredients in a dispersed form. In order to prevent the settling of the dispersed phase in suspension fertilizers, stabilizing agents like bentonite, or organic substances that increase gel viscosity and strength in suspensions, such as starch or sorbitol, are very frequently added (Rusek et al. 2009a, Das and Mandal 2015).

Thanks to the numerous functional advantages of suspension fertilizers, such as high nutrient content, improved adaptability of their composition to the needs of specific plant species, easier and more precise dosing, and better availability for plants compared to solid fertilizers, the interest in suspension fertilizers continues to grow (Rusek et al. 2009b).

It is also worth noting that it is possible to use sparingly water-soluble, less expensive phosphates for the production of suspension fertilizers. The elimination of some technological processes results in lower capital and operating costs. This is particularly advantageous when mineral acids are used as the liquid component of the formulations (Triratanaprapunta et al. 2014).

On the other hand, the introduction of suspension fertilizers requires adaptation for immediate preparation before application and spraying methods, which entails additional investments on farms. Spraying suspension fertilizers is also more troublesome compared to clear liquid fertilizers. Due to these reasons, despite attempts to introduce suspension fertilizers in Europe, they are rarely and reluctantly used. In contrast, in the United States, due to a larger scale of cultivation combined with a well-developed distribution service sector, suspensions have been successfully adopted (Górecki and Hoffmann 1995, Mikła et al. 2007, Das and Mandal 2015).

In total, the fertilizer market (including solid, liquid and suspension fertilizers) in the US, Canada and Mexico exceeded USD 26.5 billion in 2021 and is forecasted to experience an increase of 1% CAGR (Compound Annual Growth Rate) between 2022 and 2028 (Market 2022). As for the global market for liquid fertilizers, it was estimated at USD 2.5 billion in 2019 and is expected to grow by 3.7 per cent over the course of six years (Jones and Nti 2022).

In terms of consumption, after the US market, the highest demand for suspension fertilizers is observed in the European and Asian markets. The African and Middle East markets show the lowest demand due to the agrarian culture prevalent in these areas.

China accounts for approximately 25 per cent of global fertilizer production, while Russia and the United States each produce less than 10 per cent. India and Canada also have a significant share in the world fertilizer production, at 8% and 7%, respectively.

The benefits resulting from the application of suspension fertilizers, coupled with the ever-increasing demand for fertilizers, as well as the geopolitical and economic challenges, particularly those related to the economies of Russia, China or Belarus, are opening up new opportunities for manufacturers. Research into producing liquid suspension fertilizers based on waste materials is particularly intriguing in the context of the circular economy promoted by the EU. This approach aligns with environmental protection goals and addresses the depletion of natural resources, which is a growing concern (Malinowski et al. 2010, Biskupski et al. 2015, Bogusz et al. 2021).

Numerous waste materials from mining or chemical industries, along with ashes from waste mono-incineration, exhibit suitable chemical composition for fertilizer production. Waste rich in phosphorus and potassium as alternative raw materials are often difficult to use in the large-volume industry of mineral solid fertilizers. However, the production and local distribution of suspension fertilizers occur on a much smaller scale, making the diversification of waste composition, moisture content, and the presence of less soluble phosphorus compounds less of a technological problem. This diversity becomes an advantage of such renewable sources (Mikła et al. 2007, Zhou et al. 2022).

One illustrative example involves a technology using elements contained in waste, such as ashes from the combustion of sewage sludge and poultry litter. The phosphorus and potassium they contain serve as excellent substitutes for dwindling primary resources (Meng et al. 2019, Raymond et al. 2019). Achieving a suspension form involves appropriate granulation of the ashes and the addition of a stabilizing agent. What matters is that fertilizers derived from this type of waste offer the potential for longer nutrient release into the soil. Nutrients present in the liquid phase offer readily available resources for plants immediately after application. Some phosphorus compounds introduced through ashes (water--insoluble aluminum-iron phosphates) are gradually released into the soil environment (Rolewicz et al. 2016, Hauck et al. 2021, Müller-Stöver et al. 2021).

In the conducted research dedicated to suspension fertilizers using alternative raw materials, such as poultry litter ash (PLA) and sewage sludge ash (SSA), were produced. The suspension form was chosen for several reasons. Our research involving alternative raw materials such as ashes for the production of granular fertilizers (Kominko et al. 2018, Kominko et al. 2021), encountered challenges with the strength of granules. Additionally, research on phosphorus recovery from ashes highlights the popularity of extraction methods, yielding a liquid phase enriched with this component and having a low pH. Using ashes to neutralize such extracts and produce suspension fertilizers significantly improves the energy balance of the technological process. This eliminates the need for stages like of salt precipitation, filtration, granulation and drying (Smol et al. 2020).

The aim of the work was to establish the most favorable method and conditions for suspension fertilizer preparation as well as to investigate the influence of different alternative materials on the properties and content of the final product.

It was decided to prepare fertilizers dedicated for cabbage, as it has a high requirement for sulfur introduced with sulfuric acid and a comparably high potassium demand that will be provided by PLA. Phosphorus in the suspension fertilizers comes only from the alternative sources SSA and PLA (Coolong et al. 2022).

Methods and Materials

Analytical methods

To characterize raw materials and all prepared suspensions, SF1-SF6 methods described below were used.

In the solid raw materials (PLA and SSA 1 and 2) Ca, Mg, Cu, Cr, Fe, Cd, Zn, Ni, Pb and K were analyzed using Atomic Absorption Spectrometry method (Analyst 300 Perkin Elmer) after acidic digestion in concentrated hydrochloric acid or sulfuric acid following Regulation (EC) No. 2003/2003 of the European Parliament and of the Council relating to fertilizers. For the determination of Hg and As the ICP-OES method was used (Plasm 40 Perkin Elmer).

The concentration of phosphorus and its forms soluble in water and ammonium citrate was determined based on the spectrophotometric method outlined in EN 15957:2011. For the determination of total phosphorus, raw material samples were digested in a mixture of nitric and hydrochloric acid. The absorbance of the molybdenum-vanadate-phosphate complex was measured using spectrophotometer with the wavelength set at 430 nm with previously stored calibration data.

To characterize crystal phase composition in raw materials, XRD analysis was performed using a PHILIPS X'PERT PW 1830 Generator. pH measurements were conducted in a 1% solution of raw material in water, using Mettler Toledo SevenEasy pH meter.

The chemical composition of the prepared suspensions SF1-SF6 was determined using a methodology analogous to that used for raw materials. The concentrations of Ca, Mg, Cu, Cr, Fe, Cd, Zn, Ni, Pb and K were measured using AAS method after digestion in a mixture of nitric and hydrochloric acid. The various forms of phosphorus were determined using the spectrophotometric method following digestion in the same nitric and hydrochloric acid mixture. The assessment of dry matter content in the suspension fertilizer was carried out through a crystallization process using a drier. Approximately 5 g of the suspension was weighed and dried at 105°C to constant mass. In such a sample, CHNS analysis was performed using Perkin Elmer 2400 analyzer for the determination of total nitrogen and sulfur. (Additionally, XRD analysis was conducted.

In order to analyze the distribution of nutrients within the suspension fertilizers, a centrifugal separation of solid and liquid parts was carried out. Samples were centrifuged at 14500 RPM for 5 minutes. The resulting sediment was washed with acetone and then subjected to another round of centrifugation. After separation, the sediment was dried for 8 hours at 105°C. The liquid and solid phases were analyzed separately for their chemical composition using AAS and spectrophotometric methods.

The density of the suspensions was determined using pycnometric method. Three density measurements were conducted for each suspension.

The fluidity of the suspensions was assessed by measuring the time it takes for 50 ml of suspension to outflow from a cup with a 4 mm diameter outflow nozzle. Six repetitions were conducted for each suspension.

The syneresis of the suspensions was evaluated by pouring the suspension into a 25 cm^3 cylinder and observing the separation of supernatant from the suspension fertilizer after standing undisturbed for 24 h. The quantity of supernatant in the upper part of the suspension is indicative of degree of syneresis. For each suspension, 3 parallel tests were conducted, spanning a duration of 7 days. The measurements were taken at intervals of 1, 4 and 7 days. The syneresis was calculated using the following equation:

$$S = \frac{V_L}{V} \cdot 100\%$$

where: S – syneresis [%], V_L – volume of liquid in the upper part of suspension [cm^3], V – volume of suspension added to cylinder [cm^3].

The pourability was determined as a percentage as the mass of suspension poured directly from 100 cm^3 bottle after 24 h standing without disturbing and the mass of the suspension remained.

The phytotoxicity analysis of the suspensions utilized the Phytotoxkit germination test from Tigret. The test involves measuring root and aboveground growth after 3 days in comparison to a control sample. Polystyrene plates filled with a reference soil for the control test, and soil mixed with fertilizer at doses of 0.1%, 0.2% and 0.4% relative to the amount of soil (100 g).

Lepidium stivum was the chosen test plant. Ten plant seeds were evenly distributed on a paper filter placed on water-moistened soil and incubated at 25°C for 72 hours without access to light. Each type of substrate underwent the test three times. The relative percentage of seed germination (RGP), relative root growth (RRG), and germination index (GI) were calculated using the formula GI (%) = (RGP*RRG)/100.

Raw materials used in the manufacture of suspension

This paper explores the utilization of three alternative raw materials in the production of fertilizers: poultry litter ash (PLA) and two distinct ashes derived from sewage sludge (SSA). Representative samples weighing 30 kg were collected from industrial incineration plants equipped with fluid bed furnaces, located in Italy and Poland. These samples were mechanically reduced in size and then sieved. The fraction below 0.2 mm in particle size was selected for subsequent experiments.

Suspension preparation

Out of the six suspension fertilizers produced, three were based exclusively on sulfuric acid, while the remaining three were based on a blend of sulfuric and nitric acids. In each of these categories, one fertilizer was produced using PLA, another using SSA, and the last using combination of all the 3 ashes. The phosphorus present in these suspension fertilizers originates solely from the alternative sources SSA and PLA. The $N:P_2O_5:K_2O$ ratio for cabbage fertilizer should be approximately 4:1:3. To meet the potassium requirements, varying amounts of potassium hydroxide and/or potassium nitrate were incorporated into each fertilizer formulation.

There is no suspension containing solely SSA 2, primarily due to its low pH of 7.8. Initial studies have shown that using this ash alone results in a substantial increase in suspension mass and adversely affects crucial parameters such as fluidity.

Table 1 shows the exact amounts of materials used for each fertilizer.

Table 1. Materials used in production of fertilizers

	SF1	SF2	SF3	SF4	SF5	SF6
Component, g	Sulfuric acid			Acid mixture		
PLA	40.6	–	20.0	45.0	20.0	–
SSA 1	–	39.0	10.0	–	15.0	39.0
SSA 2	–	–	15.0	–	15.0	–
KNO_3	22.0	25.0	17.0	–	–	25.0
H_2SO_4	224.7	224.7	224.7	112.5	112.5	112.5
HNO_3	–	–	–	92.2	72.2	72.2
NH_3 (aq)	150.4	167.9	150.0	106.0	110.0	116.4
KOH	12.0	24.1	16.0	22.0	25.0	26.0

Suspension fertilizers were produced in 1 dm^3 stirred jacketed reactor equipped with pH-meter and thermometer.

During the initial production step, acids were mixed with water were neutralized by ammonia solution (25%) in a reactor, with a mixing speed 350 rpm, until the pH reached 0.5. In the subsequent step, all the solid ingredients were added simultaneously under mixing speed 550 rpm, and the mixture was stirred for 70 minutes. It was determined that such method and properties of the fertilizer were satisfactory. The final parameters of the suspensions were as follows: pH right after production was around 5, pH after 24 h approximately 7, and the final mass of the suspension ranged from 390 to 500 g.

Fertilizer that met the chemical and physical requirements for suspension fertilizers underwent testing on a larger scale. The tests were conducted using a stirred 5 dm^3 jacketed reactor (Globe) equipped with temperature and pH control. The tests were performed in 3 triplicate for each condition.

Results and discussion

Characterization of materials used for fertilizer production

Poultry litter ash, along with two different ashes sourced from sewage sludge (as characterized in Table 2), served as phosphorus providers and partial sources of other nutrients such as K, Mg and Ca. Sewage sludge ashes were selected from Polish wastewater treatment plants based on the highest content of phosphorus compounds. Despite containing minor quantities of heavy metals regulated by legislation, these materials were chosen due to their potential impact on production, requiring careful consideration.

The XRD analyses show that both SSA contain silicon oxide and iron oxide. Moreover, SSA1 contains calcium aluminum phosphate, whereas SSA2 contains iron phosphate and calcium iron phosphate. In PLA, the primary phase is calcium phosphate hydroxyapatite, accompanied by secondary phases such as potassium sulphate arcanite, magnesium oxide and calcium hydroxide. These results are in line with those of (Luyckx and Van Caneghem 2021).

Suspension fertilizers characterization

Physical characteristic of suspensions

During the production process, a decision was made to compromise the NPK ratio in order to neutralize the acid completely and achieve the desired pH values. It is particularly evident in fertilizers containing all 3 types of ashes. In such a complex mixture, maintaining the appropriate pH for plant growth proved to be challenging. The production ended when all the ingredients were added and pH stabilized within the range of 5 and 6 (Table 3). In most cases, pH reached 7 after 24 h and did not exceed this value. However, in the cases of SF4 and SF5, pH reached 8. This elevation resulted in the supernatant of suspension turning blue due to copper salts dissolution in the alkaline pH environment.

An easily applicable and efficient fertilizer suspension should exhibit a rapid total outflow, quantified by a pourability index of at least 98% and a fluidity that allows for the movement of 100 cm^3 of suspension between 10–15 seconds. Rheological properties, such as density, play a crucial role in the method of fertilizer application as well as the equipment used. The preferred density range is 1.20–1.40 g/cm^3. As all the solid particles of the suspension should be dispersed in the liquid phase, it is required to determine the syneresis, which confirms good stability of the suspension if its value is lower than 10% (Bogusz et al. 2021). Table 4 provides the characterization of all the aforementioned parameters for the produced suspensions.

All the fertilizers had fairly similar densities, ranging from 1.351 g/cm^3 to 1.386 g/cm^3. The pourability index displayed a notable correlation with fluidity. Suspension with the highest fluidity, such as SF1 and SF3, also showcased lower pourability indices, meeting the specified requirements. Suspension fertilizers based on sulfuric acid demonstrated reduced syneresis compared to suspensions containing acid mixture. Only SF1 and SF2 suspensions met the syneresis standard after 24h.

The process of flocculation and sedimentation, indicated by the high value of syneresis is not desirable in fertilizer suspensions. The resulting gel shrinking and the enlargement of the visible layer of liquid favor secondary nucleation. The

Table 2. Characteristic of alternative raw materials used for suspension fertilizers

Ash	pH	P_2O_5	K2O	Ca	Mg	Fe	Cu	Zn	Ni	Cr	Pb	Cd	Hg	As
	%						mg/kg							
PLA	12.0	21.8 ±0.35	15.4 ±0.85	9.68 ±0.46	6.27 ±0.03	0.78 ±0.95	644 ±19	2281 ±29	110 ±8	113 ±4	19.1 ±0.4	5.3 ±0.1	0.237 ±0.012	26.7 ±0.1
SSA 1	11.1	24.80 ±0.27	1.30 ±0.04	11.7 ±0.6	1.10 ±0.02	8.69 ±0.43	8499 ±197	2681 ±27	95 ±7	165 ±5	142 ±2	165 ±3	0.10 ±0.01	8.90 ±0.13
SSA 2	7.8	26.76 ±0.18	0.761 ±0.02	20.3 ±0.67	2.80 ±0.04	7.50 ±0.39	907 ±21	3351 ±31	55 ±4	70 ±3	117 ±2	126 ±3	<0.01	<0.10

Table 3. pH value of the suspension fertilizers

	SF1	SF2	SF3	SF4	SF5	SF6
pH	5.4	4.6	5.1	5.4	5.4	5.3
pH after 24h	7.0	6.5	7.0	8.0	8.0	7.0

growth of crystals further intensifies the sedimentation effect. In stable homogeneous suspension, significant alterations in syneresis during storage should be avoided. Consequently, an investigation into the changes in syneresis over time was performed at various intervals (1, 4 and 7 days and 1 year following preparation), as shown in Figure1.

SF1, which exhibited a syneresis of 17% after 7 days, had a fluidity of 72 seconds, and SF3, with syneresis of 23% after 7 days, had a fluidity of 65 seconds. Both of these fertilizers experienced issues with lumping. During storage, larger crystals of deposit formed at the bottom of container. On the other hand, fertilizers with the worst syneresis had the best fluidity. SF5 with a syneresis of 32% after 7 days, showed a fluidity of 15 seconds, and SF6, with a syneresis of 39% after 7 days at, had a fluidity of 14 seconds. Interestingly, these 2 fertilizers did not lump at all and could be easily stirred even after even prolonged storage. It can be noticed that suspensions based on an acid mixture (SF4-SF6) displayed more stable syneresis over the analyzed time period. In suspensions observed after one year since their separation, a reduction in syneresis was noted. All of these suspensions maintained their ease of mixing.

The results concerning the density of the obtained fertilizers and fluidity (specifically for SF2, SF5 and SF6) are in accordance with the results for NPK-type suspension fertilizers tailored for maize cultivation, utilizing waste from polyol production as a phosphorous source (Bogusz et al. 2022b). Fertilizers SF1-SF3 demonstrated better stability after 24 hours (syneresis ranging from 9 to17%) compared to fertilizers made of traditional raw materials combined with waste from polyol production and bentonite. In the latter case, delamination ranged from 20% to over 90%, depending on the fertilizer composition.

Due to the influence of the solid phase content on the rheological parameters of in the suspension, fertilizer samples were subjected to centrifugation to quantify the proportions of both phases. The results of this separation are found in Figure 2.

The reduction in the solid phase content within the suspensions influence corresponds to an increase of syneresis when using sulfuric and nitric acid. The solid phase content in the suspensions is 2–3 times greater than the initial mass of alternative raw materials introduced at the beginning of the process (ranging from 7.3 to 12.7%). This phenomenon is reflected by the results of XRD analysis of the solid phase and the alternative raw materials (Table 5). These findings confirm the reactions of its partial digestion in an acidic medium and salt precipitation in the form of calcium, magnesium and ammonium sulphates as well as potassium and calcium phosphates or potassium nitrates.

In fertilizers made only with SSA (SF2, SF6), the presence of silicon oxide or silicate is noticeable, stemming from SSA, whereas these elements are absent in PLA. Various calcium

Table 4. Pourability index, fluidity, density and syneresis of the suspension fertilizers

Fertilizer	SF1	SF2	SF3	SF4	SF5	SF6
Alternative raw material	PLA	SSA1	PLA+SSA	PLA	PLA+SSA	SSA1
Acid used	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4+HNO_3	H_2SO_4+HNO_3	H_2SO_4+HNO_3
Pourability index, %	94.3±1.3	99.2±0.3	95.1±2.1	98.7±0.5	99.1±0.5	99.4±0.4
Fluidity, s/100 cm^3	71.8±5.2	15.2±1.4	64.6±0.8	16.6±0.8	15.1±0.4	13.8±0.4
Density, g/cm^3	1.374±0.004	1.373±0.004	1.386±0.003	1.351±0.001	1.381±0.002	1.374±0.001
Syneresis after 24h, %	9.0±0.8	7.0±1.1	17±3	19±1	29±1	36±2

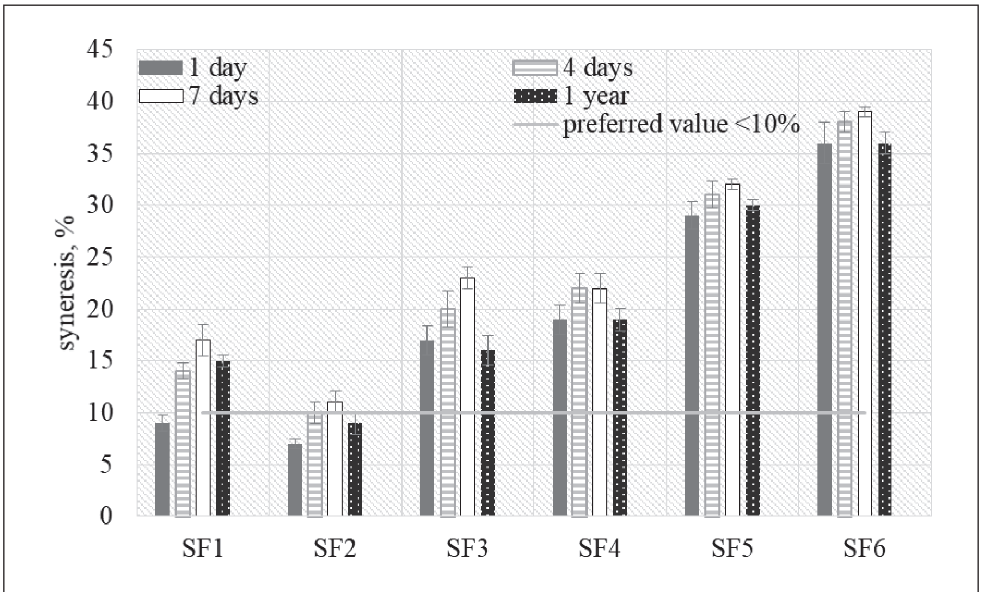


Fig. 1. Syneresis of suspension fertilizers after 1, 4 and 7 days and 1 year from its preparation

phosphate structures from ashes were either dissolved or replaced with different compounds, often incorporating nitrogen introduced through ammonia, potassium nitrate and nitric acid. In the case of SF4-SF6 (fertilizers based on an acid mixture), the presence of nitrate salts becomes apparent, a feature absent in sulfuric acid-based fertilizers. The utilization of sulfuric acid contributes to the appearance of 6 distinct sulfur-containing compounds. Iron and aluminum from ashes remained in the sediment, however usually in complex compounds.

Content of N, P, K and its distribution within the suspension

The nitrogen in fertilizers was sourced from nitric acid, ammonia and potassium nitrate. As a result, it will be available directly after application, derived from the liquid phase. Phosphorus was introduced into the suspension only through alternative raw materials, namely, ashes from poultry litter and sewage sludge. In these materials, phosphorus exists in the form of phosphate salts, often associated with Al or Fe, and these compounds exhibit limited solubility (Melia 2017). Thus, its accessibility to plants will depend on the solubility of salts and their distribution within the suspension. Similarly, potassium was partially introduced through alternative raw materials and partly as hydroxide and potassium nitrate.

Table 6 presents data on the total N, P and K content in suspensions and, additionally, it provides information on the content of these elements in the dry mass of the suspension, facilitating a more effective comparison with solid fertilizers.

Figure 3 displays the percentage of total phosphorus that is soluble in water and ammonium citrate.

Through an analysis of P and K concentrations in both the supernatant and solid phase, the distribution of P and K within suspension was assessed. The nutrients distribution across the suspension phases allows to make an initial assessment of their accessibility to plants. Components dissolved in the liquid phase will be promptly accessible to the root system. The distribution of total phosphorus and potassium within suspensions is depicted in Figure 4.

Upon viewing these data, it becomes evident that, in general, phosphorus in sulfuric acid-based fertilizers (SF1-SF3) exhibits greater solubility in water in comparison to acid mixture-based fertilizers. A notably higher proportion of phosphorus was found in the supernatants of sulfuric acid-based fertilizers (SF1, SF2 and SF3) in comparison to acid mixture-based fertilizers (SF4-SF6). Furthermore, it is worth noting that phosphorus in all fertilizers is highly soluble in ammonium citrate (pH = 7), meaning that the phosphorus will readily become available for assimilation in the soil. In

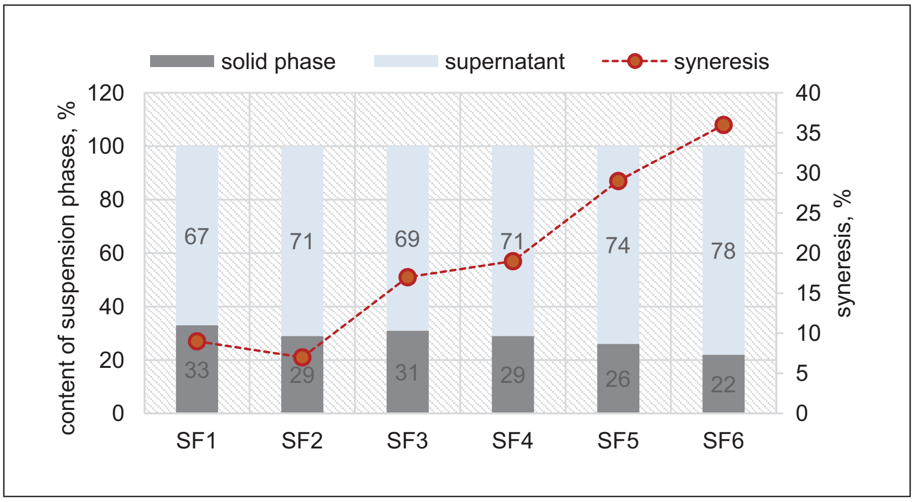


Fig. 2. Supernatant and solid phase content in suspension fertilizers in comparison with syneresis after 24 h

Table 5. Crystalline phases identified by XRD analysis in raw materials and solid phase of the suspensions

Sample	Identify crystalline phases
PLA	$Ca_9(PO_4)_6(OH)_4$, K_2SO_4, MgO, $Ca(OH)_2$
SSA 1	SiO_2, Fe_2O_3, $FePO_4$, $Ca_9Fe(PO_4)_7$
SSA 2	$SiO_{2,}$ Fe_2O_3, $Ca_9Al(PO_4)_7$
SF1	$(NH_4)_2SO_4$, $K(H_2PO_4)$, $K_2CaMg(SO_4)_3$
SF2	SiO_2, $Ca(SO_4)(H_2O)_2$, $KAlSiO_4$, $Al(PO_4)(H_2O)$
SF3	$(NH_4)_2SO_4$, $Ca_2Mg(Si_2O_7)$, KNO_3, $MgAlFeO_4$
SF4	$K(H_2PO_4)$, KNO_3, NH_4NO_3, $K_3CaH(PO_4)_2$
SF5	$SiO_{2,}$ $KAlSiO_4$, KNO_3, $K_3CaH(PO_4)_2$, $NH_4(NH_2SO_3)$
SF6	SiO_2, Fe_2O_3, $K_2CaMg(SO_4)_3$, $K(NH_4)_3(NO_3)_2SO_4$

Table 6. N, P, K content and phosphorus solubility in suspension fertilizers

Suspension fertilizer	SF1	SF2	SF3	SF4	SF5	SF6
Total N, %	6.63 ±0.03	6.97 ±0.02	7.08 ±0.03	8.39 ±0.02	8.27 ±0.02	8.59 ±0.03
Total P, % P_2O_5	1.99 ±0.01	2.09 ±0.02	3.53 ±0.12	3.30 ±0.16	2.81 ±0.12	2.41 ±0.06
Water soluble P, % P_2O_5	1.02 ±0.02	1.03 ±0.01	1.21 ±0.01	0.17 ±0.01	0.30 ±0.01	0.86 ±0.03
Ammonium citrate (pH = 7) soluble P, % P_2O_5	1.99 ±0.05	1.90 ±0.01	1.97 ±0.07	2.31 ±0.19	1.93 ±0.14	1.72 ±0.01
Total K, % K_2O	3.72 ±0.10	5.95 ±0.37	5.80 ±0.15	5.87 ±0.06	3.46 ±0.02	4.42 ±0.05
Dry matter, %	52.8	52.3	54.3	51.5	53.1	50.4
N, % in D.M.	12.56 ±0.05	13.34 ±0.04	13.04 ±0.06	16.30 ±0.04	15.57 ±0.04	17.05 ±0.06
P, % P_2O_5 in D.M.	3.77 ±0.02	4.00 ±0.04	6.50 ±0.22	6.41 ±0.31	5.29 ±0.22	4.78 ±0.12
K, %K_2O in D.M.	7.05 ±0.10	11.4 ±0.7	10.7 ±0.3	11.4 ±0.1	6.52 ±0.03	8.77 ±0.13
NPK ratio	3.3:1:1.9	3.3:1:2.9	2.1:1:1.6	2.4:1:1.8	2.9:1:1.2	3.6:1:1.83
Sum of nutrients, % in D.M.	23.38	28.74	30.60	34.11	27.38	30.60

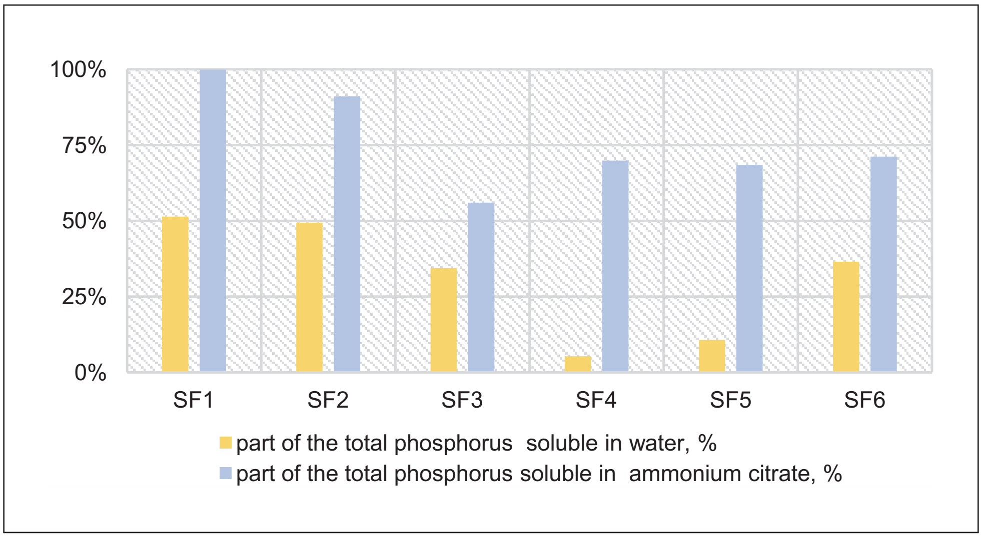
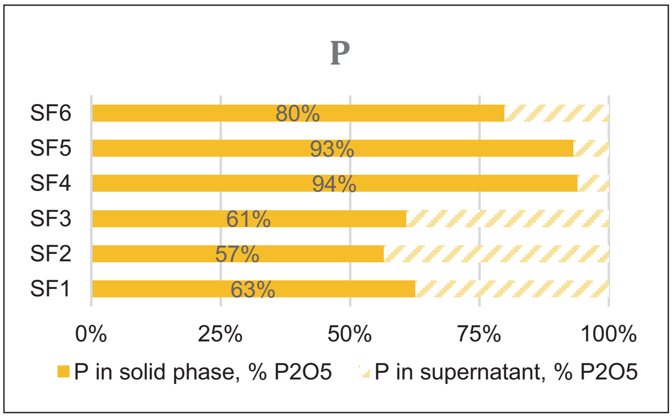


Fig. 3. Percentage of total phosphorus soluble in water and ammonium citrate



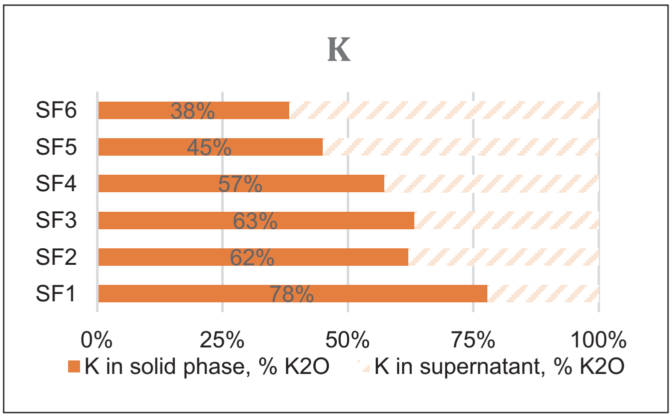


Fig. 4. P and K distribution in suspension fertilizers

terms of potassium distribution, significant quantities are concentrated in the supernatants, ranging from 22.2% in SF1 to 61.7% in SF6. Sulfuric acid-based fertilizers exhibit lower potassium distributed to the supernatant compared to acid mixture-based fertilizers.

Content of secondary nutrients (Ca, Mg, S) and microelements and its distribution within the suspension

The produced suspensions also serve as excellent sources of secondary elements and micronutrients crucial for plant nutrition (Table 7). Notably, a majority of these components (the exception is S) are entirely derived from alternative sources – namely, ashes. Taking into account the elevated costs associated with microelement fertilizers, this will have a positive effect on the final economic assessment.

Analysis of the distribution of secondary elements between the solution and the solid phase in suspension indicates that Mg compounds are mainly situated in the solid phase. The suspension with the highest concentration of Mg in the supernatant was SF2, whereas the sediment in suspension SF5 exhibited the highest concentration of Mg (Figure 5).

More than 99% of Fe and 92% of Zn are present in the solid phase. Additionally, over 80% of Cu is present in the solid phase, except for SF4 and SF5, where Cu is almost evenly distributed between both phases (Fig. 5). The limited solubility of Fe compounds in the liquid phase is confirmed by the results of the XRD analysis (Table 5), which revealed these compounds to be in the form of nearly insoluble Fe_2O_3, $FePO_4$, $Ca_9Fe(PO_4)_7$.

Table 7. Secondary elements and micronutrients concentration in suspension fertilizers

Element	SF1	SF2	SF3	SF4	SF5	SF6
	[%]					
S	9.59±0.04	8.97±0.03	8.99±0.05	9.53±0.03	5.55±0.04	5.38±0.02
Ca	3.24±0.03	0.88±0.01	2.50±0.04	3.90±0.20	3.02±0.12	1.76±0.02
Mg	0.52±0.03	0.19±0.01	0.61±0.03	0.89±0.05	0.71±0.05	0.38±0.01
Fe	0.06±0.001	0.73±0.02	0.77±0.04	0.11±0.01	0.72±0.04	0.94±0.02
	[mg/kg]					
Cu	108.9±2.2	58.2±0.2	111.5±7.9	206.8±5.1	96.7±0.1	38.2±0.1
Zn	76.4±2.6	285.8±10.1	346.0±27.7	147.1±1.9	283.9±14.2	293.7±11.0

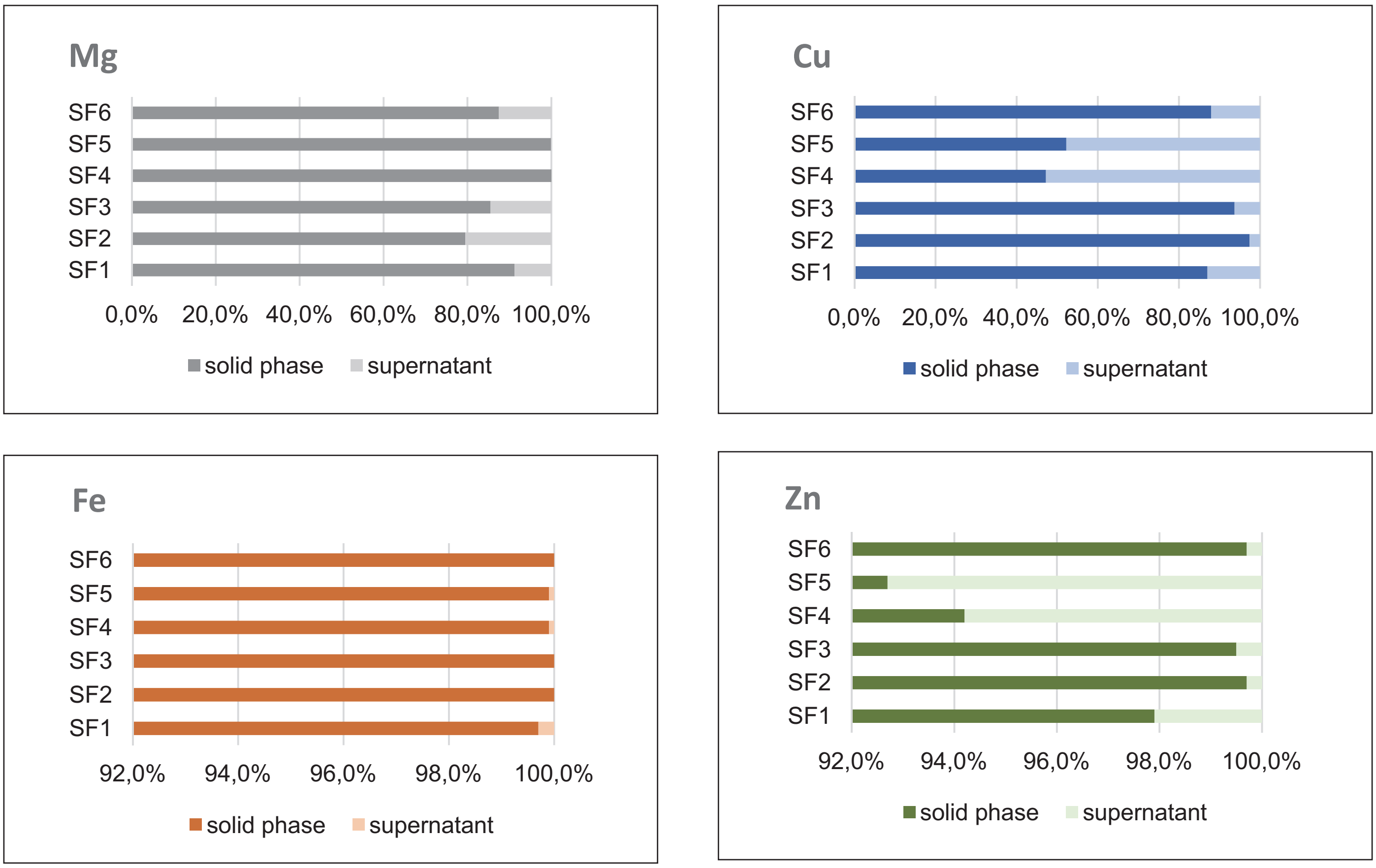


Fig. 5. Mg, Fe, Zn and Cu distribution within the suspensions phases

Content of toxic elements and its distribution within the suspension

Elements such as, Ni, Cd, Pb, Cr are introduced into the suspension fertilizer only with alternative raw materials. The content of heavy metals in fertilizers is presented in Table 8.

Most of the analyzed toxic elements limited in fertilizers are present in solid phase (Fig. 6), which indicates only insignificant digestion of raw materials in an acidic solution during the preparation of fertilizer suspensions.

Phytotoxicity of suspension fertilizers

To assess the effect of the tested product on both seed germination and root growth simultaneously, a germination index (GI) was used. As per the literature, a GI value exceeding 80%, is generally considered indicative of no observed phytotoxic effects. The content between 50–80% suggests moderate toxicity, while GI< 50 indicates a substantial phytotoxic effect (Kebrom et al. 2019).

The fertilizer doses of used in the experiments were 0.1%, 0.2% and 0.4%. The lowest dose roughly corresponds to the amount intended for application per 1 ha of cultivated area.

Based on the results from Figure 7, it can be concluded that the tested fertilizer suspensions do not show a phytotoxic effect on plant germination.

Comparison of suspension fertilizers to mineral fertilizers under new EU legislations

Produced suspension fertilizers are a very good source of nutrients and secondary elements as well as microelements.

With reference to Tables 6 and 7, a comparison can be drawn between the formulated suspension fertilizers and the solid mineral fertilizers as categorized by legislation (EU

Table 8. Toxic elements concentration in suspension fertilizers

Element	SF1	SF2	SF3	SF4	SF5	SF6
mg/kg						
Ni	16.7±0.7	32.1±0.9	26.8±0.2	27.9±0.8	21.6±0.2	21.5±1.3
Cd	0.64±0.01	0.71±0.19	0.89±0.10	0.91±0.01	0.75±0.01	0.76±0.08
Pb	4.06±0.20	12.5±0.04	5.88±0.77	0.77±0.14	8.27±0.70	6.96±0.19
Cr	7.46±0.04	12.8±0.11	11.62±0.90	11.46±0.72	16.06±0.12	15.75±0.28
Concentration of toxic elements [mg/kg of dry matter]						
Ni	31.7	39.1	49.4	54.2	40.6	42.7
Pb	7.7	14.8	10.8	1.5	15.5	13.8
Cd	1.2	1.4	1.6	1.8	1.4	1.5
Cd [mg/kg of P_2O_5]	32.1	36.0	25.1	27.4	27.0	31.4

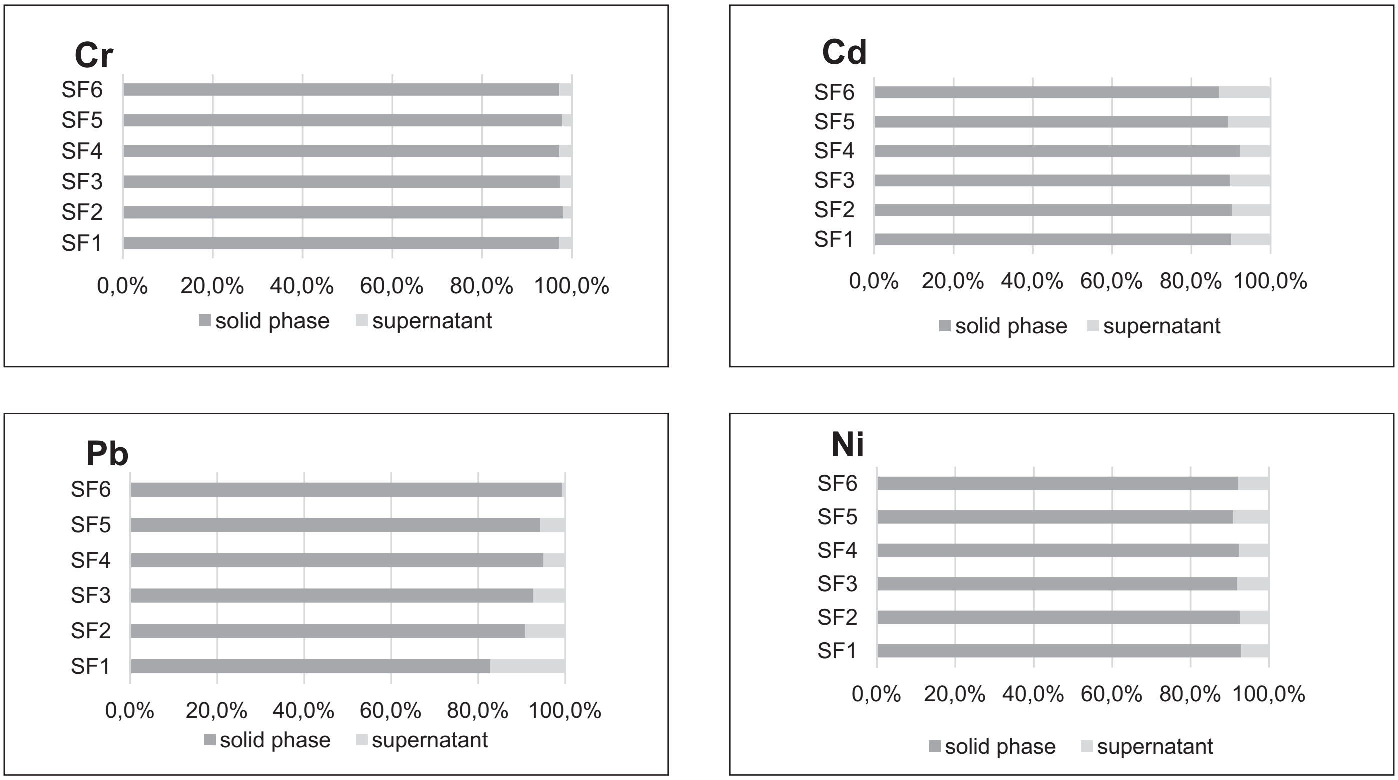


Fig. 6. Cr, Cd, Pb and Ni distribution within the suspensions phases

2019). All of the fertilizers meet the requirements for products within the function category PFC1, designed for inorganic fertilizers. Given that the produced suspensions constitute a blend of chemicals and waste-derived ash materials, they should be categorized under component material categories of CMC 1 and CMC 13, which encompass thermal oxidation materials and their derivatives. For compound macronutrient fertilizers, the minimum content of N, P and K should reach 3%, while secondary nutrients such as S, Ca, Mg should reach at least 1.5%.

The suspensions exhibit a total concentration of primary nutrients ranging from 24% to 34%, surpassing the established threshold 18%. Furthermore, all of them contain more than 3% of N and P_2O_5, K_2O thus warranting their classification as NPK fertilizers.

An undeniable advantage of the produced fertilizers lies in the utilization of alternative raw materials to introduce essential nutrients. This approach enables the inclusion of 100% of phosphorus and 1.7–30% of potassium (Figure 8). For secondary nutrients, their concentration in fertilizers can be declared if it surpasses the threshold of 1.5%. All the suspensions contain S level that exceeds this requirement.

Despite the incorporation of ashes from waste combustion, such as poultry litter or sewage sludge, into the suspension fertilizers, which contain metals regulated in fertilizer products, the levels of these metals have not been surpassed (Table 8). The concentration of nickel falls within the range of 31.7–54.2 mg/kg dry matter (below the limit 120 mg/kg dry matter), while lead concentration is measured at 1.5–15.5 mg/kg dry matter (below the limit of 150 mg/kg dry matter). Cd concentration ranges from 1.2 to 1.8 mg/kg dry matter and Cd mg/kg P_2O_5 is 25.1–36 mg/kg P_2O_5 (both below the limit of 3 mg/kg dry matter and 60 mg/kg P_2O_5, respectively).

Technological, economic and environmental assessment

The results indicate that the fertilizer that successful fulfills all physical and chemical requirements for dedicated suspension fertilizer is the one derived from SSA and sulfuric acid (SF2). This suspension possesses a combined nutrient content of 28.74%, with a nutrient ratio (NPK) of 3.3:1:2.9. This ration closely aligns with the nutrition demand of cabbage, which demands a ratio of 4:1:3. Furthermore, SF2 demonstrates stability with a syneresis of 7.0, high pourability index of 99.2%, and a normative fluidity of 15 s/100 cm^3.

This composition was chosen for production on a larger scale to validate the repeatability of the production process. The obtained fertilizers exhibited consistent composition and physicochemical parameters, which did not differ by more than 1%.

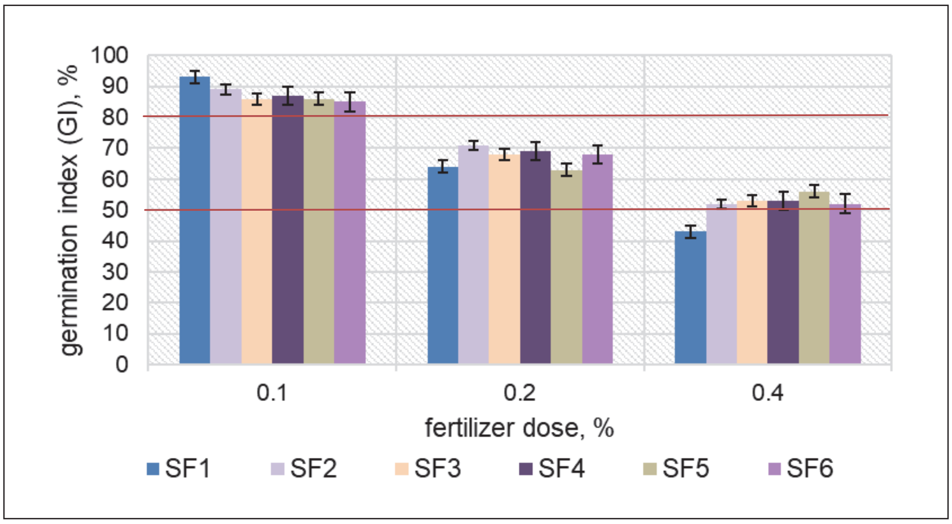


Fig. 7. Germination index for fertilizers dose 0.1%, 0.2% and 0.4%

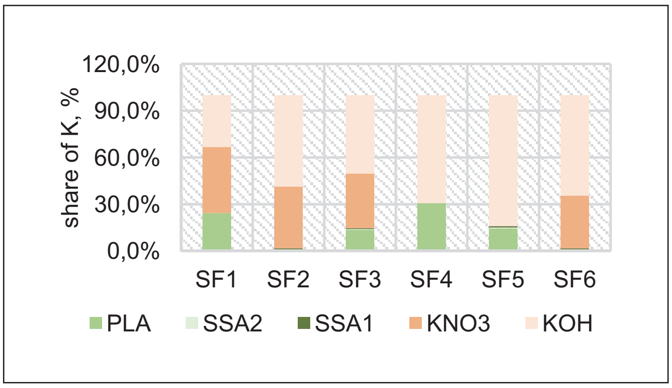


Fig. 8. Share of P and K introduced to suspensions with alternative raw materials (PLA, SSA) and other chemicals

Based on these data, a mass balance of the production process was established, and the raw material cost of its manufacture was estimated. To produce 1 Mg of suspension fertilizer, the following quantities of raw materials are required: 79.5 kg of SSA, 50.95 kg of KNO_3, 457.94 kg of sulfuric acid, 342.12 kg of 25% ammonia solution, 49.12 kg of KOH and 20.38 kg of water. Considering these quantities and assuming that the ash obtained after sludge incineration is required at no cost, the total cost of these materials would amount to 323 €. The prices of raw materials are estimated as follows: potassium nitrate (787 €), sulfuric acid (65 €), ammonia water (263 €) and potassium hydroxide (3650 €). The average prices of raw materials are based on specific quotations received from manufacturers during the period of June to September 2022.

On the other hand, the value of NPK components and microelements introduced by suspension fertilizer should be considered. The prices of microelements are much higher than those of simple nutrients, and in the case of manufactured suspensions, they come in 100% from renewable sources, which is a big advantage of such fertilizers on the market.

According to market analysis, the average price of NPK in 2019 was as follows: 1.71 €/kg of nitrogen, 1.65 €/kg P_2O_5 and 0.90 € per kg of K_2O. Depending on the form of micronutrients (solid or liquid) their prices fluctuate to a certain extent, but the following average prices were used for analysis: 46 € per kg of Cu, 31 € per kg of Zn and 52 € per kg of Fe. The market value of all the above components (assuming complete plant availability) contained in 1 Mg of suspension fertilizer was therefore estimated at 596 €. This value is much higher than the costs of raw materials taken for the production process.

It can, therefore, be inferred that the ultimate price of a suspension fertilizer, based on renewable raw materials rich in macro- and micronutrients, is likely to be competitive on the market of fertilizers. Presently, fertilizer prices range from approximately 400–720 euros per Mg of solid compound fertilizer.

The production of suspension fertilizers takes on an environmental perspective by effectively managing the waste generated from sewage treatment plants in the form of sewage sludge ash. In this context, the sewage treatment plant from which the ash was sourced generates approximately 900 Mg of SSA per year. A comprehensive ash management approach from this treatment plant could yield the production of 11,323 Mg of suspension fertilizer and the recovery of 233 Mg of phosphorus compounds.

Conclusions

Alternative raw materials in the form of sewage sludge ash or poultry litter ash are viable substitution of fossil phosphates in production of fertilizers. Sewage sludge ashes are rich in phosphorus (even up to 27% of P_2O_5), and poultry litter ash is rich in both phosphorus and potassium (22% P_2O_5 and 15.5% K_2O).

The production of suspension fertilizers has led to the creation of NPK fertilizers with a total concentration of primary nutrient in dry mass ranging from 23% to 34% ($N+P_2O_5+K_2O$). These fertilizers are abundant in secondary nutrients and microelements, all while adhering to the specified regulations for toxic metals content.

The most suitable dedicated suspension fertilizer for cabbage was formulated using sewage sludge ash, along with sulfuric acid, ammonia, potassium nitrate and potassium hydroxide. The composition of primary nutrients (within the suspension) stood at 7% N, 2.1% P_2O_5 and 3.9% K_2O. The suspension was also enriched with secondary nutrients, comprising 3.2% Ca, 0.5% Mg and 8.9% S. This particular formulation demonstrated a syneresis of 7.0%, an impressive pourability index of 99.2%, a normative fluidity of 15 s/100 cm^3 and a density of 1.372 g/cm^3.

Fertilizers produced using poultry litter ash exhibited a tendency to form larger lumps during storing. Conversely, suspensions produced with sewage sludge ashes had fine size of sediments.

A clear advantage of the produced suspension fertilizers lies in the utilization of alternative raw materials to introduce primary nutrients, including 100% of phosphorus and 1.7–30% of potassium.

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