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Fertilization with Municipal Wastewater Phosphorus Adsorbed to Alginate Beads: Results from a Pot Experiment with Italian Ryegrass

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Abstract: The global increase in the demand for fertilizers and thus phosphorus (P) contributes to the depletion of P reserves and the need to recycle this element. This paper presents the results of a pilot-scale experiment on the possibility of using a fertilizer preparation containing alginate, Fe and P (AFP) obtained in the process of P adsorption from sludge water on a hydrogel alginate adsorbent cross-linked with iron (III) ions. The influence of AFP on the growth of a model plant of the Italian ryegrass (*Lolium perenne* cv. Turtetra) was examined in comparison with differentiated mineral fertilization (MF) under the conditions of a pot experiment. The two fertilizers produced similar crop yields of the tested plant and had similar plant and soil macro- and micro-elements, except for the content of Fe and Cu in ryegrass, which was significantly higher with AFP fertilization. Further research on the use of the proposed sorbent for large-scale P recycling in an uncontrolled field environment should include acceptable limits for multivalent metal concentrations in wastewater, the mechanical/thermal stability, and the effectiveness of AFP under field conditions and a cost competitiveness. AFP has the potential to compete with mineral fertilizers for P fertilization, and this technology is in line with the EU circular economy vision.

Keywords: phosphorus removal; wastewater; alginate adsorbents; fertilizer formulation; multivalent metals



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1. Introduction

The intensification of food production generates increasing use of phosphate fertilizers, which on a global scale is at the level of 14 million t P/year [1]. Modern agriculture is dependent on phosphorus (P) derived from phosphate rock, which is a non-renewable resource. It is estimated that economically viable sources may be depleted in 50–100 years [2], while a review of the global resources of phosphate rock undertaken by the International Fertilizer Development Center showed that this is notably longer—between 300 and 400 years [3]. While the timing of the production peak may be uncertain, the fertilizer industry recognizes that the quality of existing phosphate rock is declining. Additionally, phosphate rock reserves are far from equally spread around the world, with three-quarters located in Morocco and Western Sahara [4]. Thus, the prospect of P shortages and depletion ultimately threatens global food security, and regions of insufficient soil nutrition levels are especially vulnerable [2,5]. Much of P is dispersed in the environment, approximately 55% of P in food is lost between “farm and fork” [6] and close to 25% of the billion tons of P mined since 1950 has ended up in water bodies [2,7]. The natural riverine load of P has doubled, this has led to eutrophication of lakes and coastal areas and will continue to have an impact for several thousand years [1,7]. Therefore, recovery and reuse of P within the human food chain are highly desirable [1–3,8].

A model of the global potential of P fertilizer recovery from wastewater showed that humans discharge a maximum of 3.7 Mt total phosphorus (TP) into wastewater, which could potentially satisfy 20% of the global fertilizer demand [5]. In Central Europe, municipal wastewater contains a P load that could theoretically replace 40 to 50% of the annually applied mineral P fertilizer in agriculture [9]. Products of wastewater treatment, e.g., sewage sludge, which additionally contain other macro and microelements as well as organic matter, are a significant source of P. One ton of dry sewage sludge contains on average 8 kg of P, 6 kg of N, 200 kg of organic matter and 10 kg of different soluble salts [10]. The main limitation in recycling P in the form of sewage sludge, is the lower availability of P for plants compared to mineral fertilizers [1,11], possibility of introducing toxic metals and pathogens into the soil environment [12] as well as the necessity to monitor the composition of soil and sewage sludge for contaminants [10]. In the process of sludge neutralization, even 60% of the P removed from wastewater can be re-released into the sludge liquid. An exemplary concentration can be up to 435 mgP/L in sludge liquid from gravity thickeners and up to 590 mgP/L from fermentation chambers [13]. Ignoring economic and legal realities, it can be presumed that the best source of P for plant nutrition is sludge water [14].

P recovered from liquid phase can be achieved via biological assimilation and physico-chemical mechanisms, including precipitation, membrane separation, reduction, extraction, ion exchange, and adsorption [15,16]. Chemical precipitation is the most common and cost-effective process used to remove P; it can remove 80–99% P in wastewater streams in the form of struvite [14,17]. This technology requires alkalinity and pH control and leads to increased sludge production [18,19]. Alternative, simple and cheap methods of P recovery are therefore sought. The adsorption process can reduce P to trace or non-detectable concentrations, with minimal waste production and high reusability [20]. Many materials have been suggested as P adsorbents, but competitive foreign ion adsorption, the high cost of regenerating solutions, and the sorbents themselves present challenges for full-scale implementation [15]. These limitations are more minor in the case of using the adsorbent containing alginate and Fe (AF) obtained by cross-linking alginate with iron(III) chloride [21]. Alginates are natural polysaccharides obtained from mainly brown algae, and they are fully biodegradable components of their cell walls [22]. After introduction into soil, alginates affect the physiological activity of the plant, they increase germination activity, extend shoots and stimulate the growth of roots and plants [23,24]. Additionally, they improve the physical properties of the soil by delaying the dissolution of fertilizers, increasing the efficiency of water use, and reducing erosion [25]. Na-salt of alginic acid with Fe(III) cation forms structures with a large specific surface [26,27] and anionic sorption capacity. By such modification using Fe(III) or Zr(IV) compounds, adsorbents were obtained for purifying water from oxyanions containing Se(IV), Cr(VI), and As(V) [27,28] or P(V) [21,29]. After P adsorption, the alginate hydrogel beads, cross-linked with Fe(III) ions can be used as a slow-release fertilizer preparation containing alginate, Fe and P (AFP) without any additional processing. This solution is in line with the most sought-after methods of recovery of P from wastewater in a form suitable for use as a fertilizer [2,3].

In this work, preliminary application studies on the possibility of using AFP as fertilizer were conducted. The fertilizer preparation was obtained in P adsorption from seepage water (SW) collected during the dewatering of sewage sludge in a mechanical and biological sewage treatment plant. It was hypothesized in this study that alginate formulation AFP would perform equally or better than mineral fertilizer (MF) in pot trials with Italian ryegrass (*Lolium perenne* cv. Turtetragrowth). Since the adsorption of P on alginate adsorbents is competitive with the adsorption of polyvalent metals [30–32], the study also investigated the effect of the tested fertilizers on the content of selected polyvalent metals in the plant and soil.

2. Materials and Methods

2.1. Preparation of AFP

Alginate matrices, cross-linked with Fe(III) ions (AF), with bead size 2.5–3.0 mm used as an adsorbent, were prepared according to the method described by Siwek et al. [21]. Interaction between alginate and Fe(III) ion is explained by a side binding model where Fe(III) ions are bound to binding sites in the alginate and form spatially separated iron (III) centers on the alginate backbone [26]. The course of adsorption of phosphates and the changes in pH, indicate that the process of removing P by AF beads generally consists of adsorption on a large specific area [21].

AF beads were saturated with phosphate ions in seepage water (SW) from a sewage sludge press in the mechanical and biological sewage treatment plant in Nowogard (Poland, West Pomeranian Voivodeship). For this purpose, 2.0 L of AF was placed in 50 L of SW with 81 mgP/L content. The adsorption process was carried out for five days at room temperature. After the adsorption was completed, the obtained AFP preparation was rinsed with water and stored in distilled water under cool conditions (4 °C). The characteristics of the AFP, which contained about 98% water are summarized in Table 1.

Table 1. The content (g/kg) of selected components of the AFP fertilizing preparation.

Alginate	Fe	P	Cu	Pb	Zn	Cd
17.96	4.04	2.37	0.214	1.122	1.947	0.0822

2.2. Plant Cultivation

The pot experiment was established at the beginning of June 2019 in the experimental station (vegetation hall) of the West Pomeranian University of Technology in Szczecin. Plants were grown in the open air, with sunlight through a foil roof, which protected the plants against uncontrolled access to rainwater. The two-factor pot experiment was set up in triplicate in a complete randomization design. The first-order factor was the dose of P, three levels of fertilization: 0.136, 0.271, 0.407 g P per pot, and per hectare: 30, 60, and 90 kg P. The second-order factor was two types of P fertilizer: the AFP hydrogel preparation and the MF superphosphate. Nitrogen (N) and potassium (K) fertilization was applied in an undifferentiated dose to all research objects in the amount of 140 kgN/ha and 120 kgK/ha. Before filling the pots, the soil was sieved through a mesh size of 2 cm to aerate and loosen it [33]. The soil material used has the composition of fine-grained clay sand. PVC pots were filled with soil material weighing 13.15 kg. Then, appropriate amounts of AFP and MF were introduced into the pots. The test plant was Italian ryegrass cv. Turtetra. The seeds of the test material were sown manually, 40 seeds per pot. The water moisture of the substrate was maintained throughout the growing season to 200 mbar/h Pa using the Stelzner 8060 tensiometer placed at a depth of 20 cm.

2.3. Soil and Plant Material Sampling

The first mowing was carried out eight weeks after the full emergence of the plants in the initial heading stage (cut I). Cut II was six weeks after cut I, and cut III was six weeks after cut II. The experiment was completed at the end of October 2019 and lasted 5 months.

The fresh weight yield was weighed after each cut. To determine the dry matter yield and the content of essential chemical components, the samples were dried at 70 °C [34]. Biometric measurements (height of shoots, length and width of leaf blades) were taken during the harvest of plants. The width and length of the leaf blades were determined on the second (from the bottom) fully developed leaves [35]. After the last cut, soil samples were taken using an Egner cane, in which the content of basic minerals was determined [36].

2.4. Analytical Procedure

The plant material from each cut was ground to a fraction below 0.2 mm and the moisture content was determined using the drying method from [37]. Total carbon (TC)

and total nitrogen (TN) content were determined using a Thermo Fisher Scientific Flash SMART elemental analyzer. For further analyses, plant samples were mineralized in a mixture of HNO₃ and HClO₄ (3:1). The total phosphorus (TP) content was determined by spectrophotometry at a wavelength of 436 nm on a UV/Vis Thermo Scientific Evolution 201 spectrophotometer [38]. The metal content was determined on the Solar S4 atomic absorption spectrophotometer with air-acetylene flame atomization at the following wavelengths: $\lambda_{Zn} = 213.9$ nm, $\lambda_{Cd} = 228.8$ nm, $\lambda_{Cu} = 324.8$ nm and $\lambda_{Pb} = 217.0$ nm.

Chemical analyses of the soil were performed one week before planting and one week after the end of the experiment. Soil pH was determined potentiometrically in water (pH_{water}) suspension and KCl solution (pH_{KCl}) using an Elmetron CX-505 pH meter [39]. Salinity-specific conductivity (SC) was determined conductometrically using WTW Cond 730 [39]. The elemental composition of the soil was determined using the same methods as with the plant material, after prior mineralization in a mixture of HNO₃ and HClO₄ (1:1) [40]; graining (once), for the skeleton fraction and sands by the sieve method, for the finer fractions using the Bouyoucos areometric method modified by Casagrande and Prószyński [41]. The available P in the soil (AP) was extracted with Mehlich-1 solution containing 0.05 M HCl + 0.0125 M H₂SO₄ and determined by spectrophotometry using a UV/Vis Thermo Scientific Evolution 201 spectrophotometer [42].

Leaf and stem length measurements were made using a ruler with an accuracy of 0.1 cm. The width of the first leaf was measured at half leaf length. For this purpose, an electronic caliper CD-15APX (Mitutoyo) was used, enabling measurement with an accuracy of 0.01 mm. Fresh and dry mass (DM) of the above-ground part was determined using a laboratory balance AD1000 (Axis) with an accuracy of 0.01 g [35].

2.5. Statistical Analysis

Two-way analysis of variance (ANOVA) was carried out to determine statistically significant differences between treatments (at $p < 0.05$). Homogeneous groups for the examined treatments were determined by Tukey's (HSD) multiple-comparison test. Statistical analyses were carried out using the Statistica PL 13.1 software.

3. Results

3.1. Grass Yields

Types of P fertilizers (the AFP hydrogel preparation and the superphosphate MF) and applied doses (30, 60, and 90 kgP/ha) influenced the differentiation of germinated seeds of Italian ryegrass (Figure 1). The highest sprouting was found for both fertilizers at the lowest P dose of 30 kg/ha and the lowest sprouting for the highest dose of 90 kg/ha (Figure 1). A more significant share of sprouted seeds was found on the objects fertilized with MF for which it was on average 54%, while in the case of AFP fertilization, it was 40%. These differences were not significant as the obtained results were within the range of calculated standard deviations. The exception was sprouting at a dose of 60 kgP/ha, where AFP was much lower than MF. Standard deviations for individual MF doses ranged from 2 to 4%, while for AFP the deviations were greater at 6 to 14%.

The assessment of the effect of the type of fertilization on the morphological features of the plants harvested in cut I showed no significant differences comparing most cases except for the length of the stem, which was significantly longer for AFP at 60 mgP/ha (Table 2). In subsequent cuts, higher values of the studied features were found for AFP fertilization too, longer leaves were observed in cuts II and III at 30 mgP/ha and wider leaves were found for all doses of AFP in cut II and for doses 30 and 90 mgP/ha in cut III. For both fertilizers, all tested morphological parameters decreased with the age of the plants. Mean leaf lengths in cuts I, II and III were 34, 31 and 19 cm, respectively, for MF and 35, 34 and 19 cm for AFP. For both types of fertilization, in cuts I, II and III, mean leaf widths were 7, 6 and 4 mm, and mean stem lengths were 7, 4 and 3 cm, respectively.

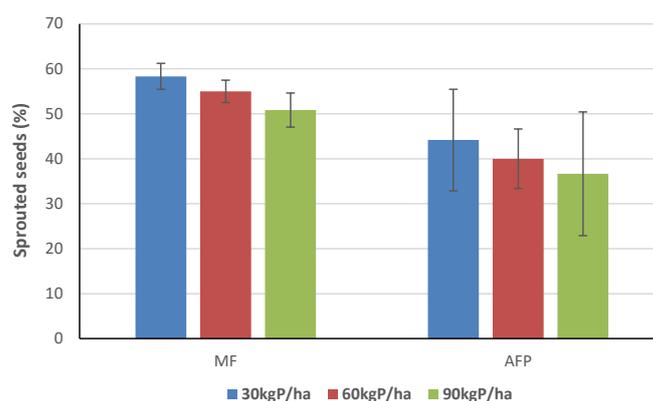


Figure 1. The number of Italian ryegrass seeds that sprouted depending on the type and amount of fertilization. MF—mineral fertilizer; AFP—hydrogel capsules with adsorbed P.

Table 2. Size of leaf length and width and stem length in three successive cuts of Italian ryegrass depending on the type and amount of fertilization.

Cut	Dose kgP /ha	Leaf Length (cm)		Leaf Width (mm)		Stem Length (cm)	
		MF	AFP	MF	AFP	MF	AFP
I	30	32.54 ^{a,X}	33.17 ^{a,X}	7.56 ^{a,X}	7.59 ^{a,X}	6.31 ^{a,X}	6.30 ^{a,X}
	60	35.67 ^{b,X}	37.26 ^{b,X}	7.57 ^{a,X}	7.67 ^{b,X}	6.49 ^{a,X}	7.18 ^{b,Y}
	90	33.08 ^{a,X}	34.82 ^{a,X}	7.51 ^{a,X}	7.14 ^{c,X}	6.89 ^{b,X}	7.31 ^{a,X}
II	30	26.35 ^{d,X}	33.65 ^{d,Y}	5.79 ^{d,X}	6.37 ^{d,Y}	3.94 ^{d,X}	4.10 ^{d,X}
	60	34.57 ^{e,X}	36.20 ^{e,X}	6.57 ^{e,X}	6.61 ^{d,X}	4.72 ^{e,X}	4.18 ^{d,Y}
	90	32.49 ^{f,X}	32.31 ^{d,X}	6.14 ^{f,X}	6.41 ^{d,Y}	4.61 ^{e,X}	4.81 ^{e,X}
III	30	17.11 ^{g,X}	19.60 ^{g,Y}	3.74 ^{g,X}	4.53 ^{g,Y}	2.47 ^{g,X}	2.46 ^{g,X}
	60	20.47 ^{h,X}	17.84 ^{h,Y}	4.69 ^{h,X}	4.22 ^{h,Y}	2.91 ^{h,X}	2.90 ^{h,X}
	90	19.45 ^{i,X}	19.47 ^{g,X}	4.41 ^{i,X}	4.56 ^{g,Y}	3.01 ^{h,X}	3.01 ^{i,X}

a, b, c—significant differences between doses in cut I; d, e, f—significant differences between doses in cut II; g, h, i—significant differences between doses in cut III; X, Y—significant differences between fertilizers with the same dose; MF—mineral fertilizer; AFP—hydrogel capsules with adsorbed P.

Similarly, with each subsequent mowing, the yield of the Italian ryegrass decreased (Figure 2). The amount of AFP dose had no effect on relative yield for the specific cuts. For MF, yield was significantly lower at 60 mgP/ha compared to the other two doses. The exception was the yield in cut III, which was comparable for all applied doses of MF.

3.2. Grass Chemical Properties

In the MF fertilization trial, mean TP plant content increased with the dose level as follows: 1554, 1578 and 1632 mgP/kgDM at 30, 60 and 90 kgP/ha, respectively (Figure 3A). For ryegrass fertilized with AFP, mean TP was highest at 60 kgP/ha reaching 1670 mgP/kgDM. For the other two doses, it was comparable reaching 1583 and 1557 mgP/kgDM at 30 and 90 kgP/ha, respectively.

The highest TP content was found in grass from cut I at a fertilizer dose of 60 kgP/ha, amounting to 1758 and 1725 mgP/kgDM for MF and AFP, respectively (Figure 3A). Significant differences in TP plant content were found in the subsequent cuts at 60 and 90 kgP/ha for MF and AFP. Although, in this analysis, many significant differences were found between the individual treatments and doses, the average TP content calculated for the entire yield was comparable and amounted to 1588 and 1603 mgP/kgDM for MF and AFP, respectively.

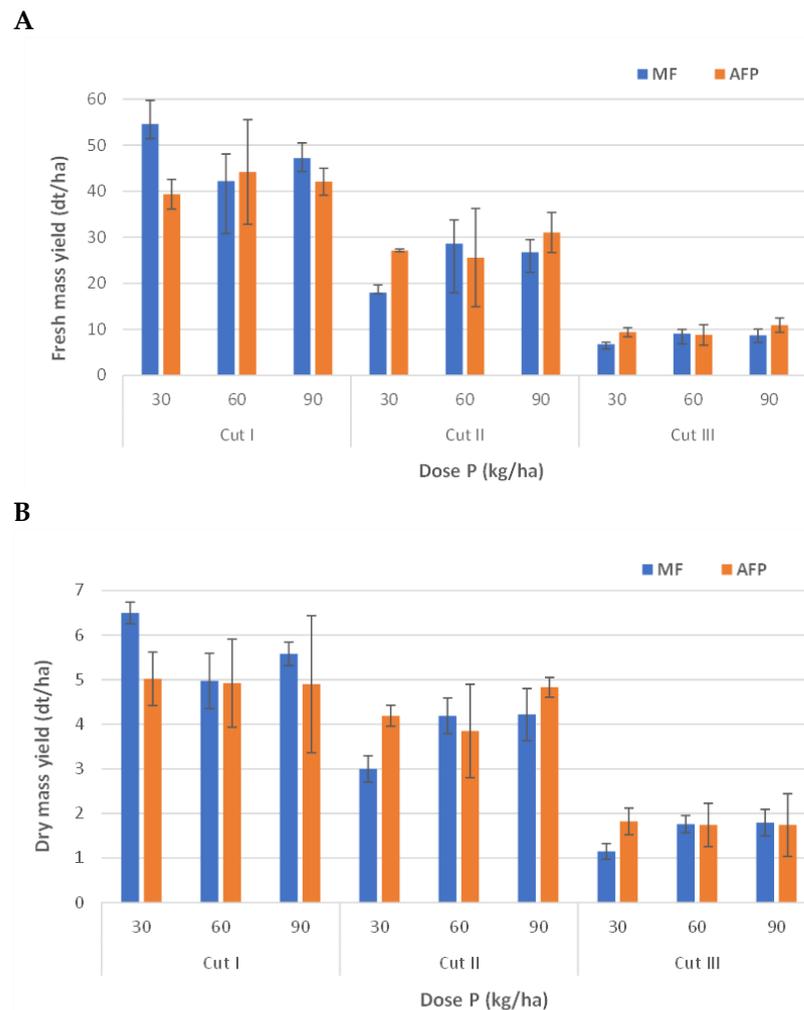


Figure 2. Yield of ryegrass mass depending on the cut and the type and amount of fertilization ((A)—fresh mass; (B)—dry mass). MF—mineral fertilizer; AFP—hydrogel capsules with adsorbed P; dt/ha—decitonne/hectare.

TN content decreased with the age of the plants (Figure 3B). The mean contents of TN in individual cuts I, II and III were 1.6, 0.7 and 0.4% DM, respectively, for plants fertilized with MF. TN was 1.7, 0.7 and 0.5% DM, respectively, for plants fertilized with AFP. No significant influence of the tested factors on TC plant content was found (Figure 3C).

For both types of fertilizer, the highest Zn and Cu content was found in cut I. In subsequent cuts, the content of these elements was lower (Table 3). The highest Fe content was found in cut III. For the other tested metals, the content levels were comparable throughout the plant growth period. Cu and Fe plant content in cuts I and II was elevated in the AFP treatment. Fe plant content in cut III was elevated in the MF treatment. The content of other metals in the plant varied to a small extent, in the case of Pb from 3.2 to 7.3 mg/kgDM in the MF treatment and from 2.6 to 4.8 mg/kgDM in the AFP treatment. In the case of Cd, these ranges were from 2.2 to 3.7 and from 2.2 to 3.3 mg/kgDM, respectively.

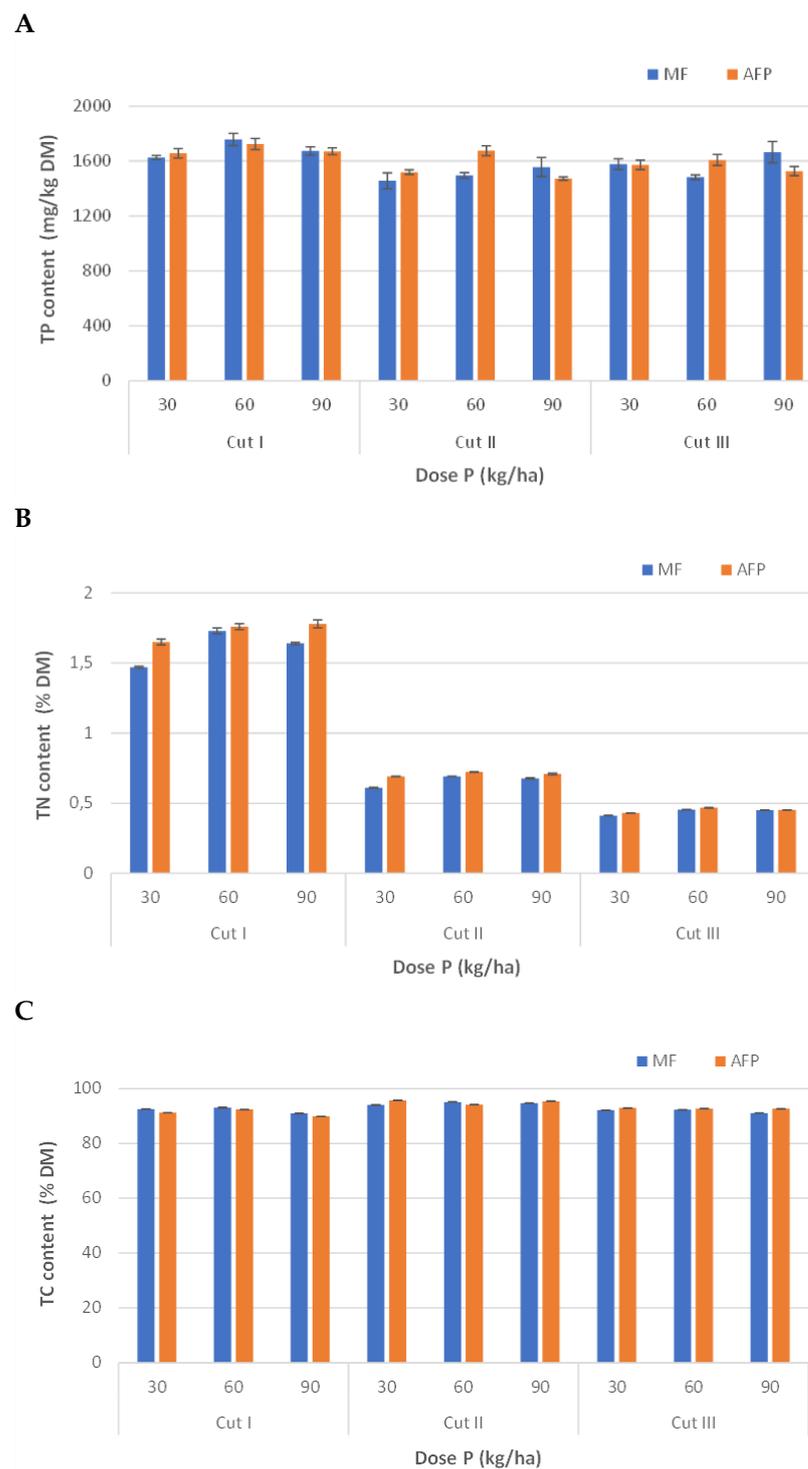


Figure 3. The content of phosphorus, nitrogen and carbon in Italian ryegrass depending on the cut and the type and amount of fertilization ((A)—TP content; (B)—TN content; (C)—TC content). MF—mineral fertilizer, AFP—hydrogel capsules with adsorbed P.

Table 3. Metal content in Italian ryegrass depending on the cut and type and amount of fertilization.

Cut	Dose kgP/ha	Metal (mg/kgDM)									
		Fe		Pb		Cu		Cd		Zn	
		MF	AFP	MF	AFP	MF	AFP	MF	AFP	MF	AFP
I	30	430 ^{a,X}	611 ^{a,Y}	5.2 ^{a,X}	4.8 ^{a,X}	16.9 ^{a,X}	18.2 ^{a,Y}	2.7 ^{a,X}	3.2 ^{a,Y}	188 ^{a,X}	258 ^{a,Y}
	60	366 ^{b,X}	470 ^{b,Y}	3.2 ^{b,X}	2.6 ^{b,Y}	17.7 ^{b,X}	19.3 ^{b,Y}	3.5 ^{b,X}	3.13 ^{b,Y}	234 ^{b,X}	221 ^{b,X}
	90	468 ^{c,X}	634 ^{a,Y}	4.9 ^{a,X}	4.7 ^{a,X}	17.2 ^{a,X}	19.5 ^{c,Y}	3.6 ^{c,X}	3.03 ^{c,Y}	221 ^{c,X}	207 ^{c,X}
II	30	423 ^{d,X}	456 ^{d,Y}	6.6 ^{d,X}	3.4 ^{d,Y}	11.0 ^{d,X}	12.0 ^{d,Y}	2.2 ^{d,X}	2.7 ^{d,Y}	106 ^{d,X}	119 ^{d,Y}
	60	327 ^{e,X}	414 ^{d,Y}	5.7 ^{e,X}	3.2 ^{d,Y}	11.3 ^{e,X}	13.1 ^{e,Y}	2.4 ^{e,X}	2.3 ^{e,X}	109 ^{d,X}	115 ^{e,X}
	90	468 ^{d,X}	379 ^{e,Y}	7.3 ^{d,X}	4.2 ^{e,Y}	10.5 ^{d,X}	11.4 ^{f,Y}	2.5 ^{f,X}	2.2 ^{f,Y}	115 ^{e,X}	109 ^{f,Y}
III	30	833 ^{g,X}	716 ^{g,Y}	5.7 ^{g,X}	4.0 ^{g,Y}	7.9 ^{g,X}	6.9 ^{g,Y}	3.7 ^{g,X}	3.3 ^{g,X}	136 ^{g,X}	142 ^{g,X}
	60	766 ^{h,X}	447 ^{h,Y}	4.3 ^{h,X}	2.6 ^{h,Y}	7.0 ^{h,X}	7.8 ^{h,Y}	3.3 ^{g,X}	3.2 ^{g,X}	121 ^{h,X}	131 ^{g,Y}
	90	745 ^{h,X}	649 ^{i,Y}	3.8 ^{i,X}	3.1 ^{i,X}	6.6 ^{i,X}	7.7 ^{i,Y}	3.3 ^{g,X}	3.3 ^{h,X}	123 ^{h,X}	117 ^{h,Y}

a, b, c—significant differences between doses in cut I; d, e, f—significant differences between doses in cut II; g, h, i—significant differences between doses in cut III; X, Y—significant differences between fertilizers with the same dose; MF—mineral fertilizer; AFP—hydrogel capsules with adsorbed P.

3.3. Impacts on Soil Chemical Properties

Soil TN content was the same before and after the experiment and amounted to 0.13%. For TC, it was 2.29% before the experiment and 2.24 to 2.33% afterwards.

The applied fertilizers significantly influenced the content of the tested forms of P in the soil, which increased by the end of the experiment (Table 4). The content of TP after the application of MF and AFP increased by 66% and 70%, respectively. Both fertilizers had a smaller effect on the soil-AP content, which increased on average by 47% with the application of MF and 38% with the application of AFP.

Table 4. Soil chemical composition as a function of fertilizer type and dose.

Fertilizer	Dose (kgP/ha)	P Content (mg/kgDM)		Microelements Content (mg/kgDM)					SC (μS/cm)
		TP	AP	Fe	Pb	Cu	Cd	Zn	
Non	0	213.0	8.5	270.0	31.0	19.0	2.02	385.0	252
	30	350.0 ^{a,X}	11.5 ^{a,X}	260.4 ^{a,X}	30.2 ^{a,X}	18.4 ^{a,X}	1.46 ^{a,X}	301.9 ^{a,X}	198
MF	60	356.3 ^{a,X}	13.1 ^{b,X}	255.4 ^{b,X}	29.1 ^{a,X}	16.3 ^{b,X}	0.99 ^{b,X}	281.9 ^{a,X}	218
	90	346.9 ^{a,X}	12.9 ^{b,X}	250.3 ^{b,X}	28.3 ^{a,X}	17.9 ^{c,X}	1.24 ^{c,X}	290.7 ^{a,X}	185
AFP	30	370.3 ^{d,Y}	12.1 ^{d,Y}	254.2 ^{d,Y}	28.1 ^{d,Y}	17.4 ^{d,Y}	1.21 ^{d,Y}	284.0 ^{d,Y}	187
	60	356.0 ^{e,Y}	11.8 ^{e,Y}	257.4 ^{e,Y}	26.2 ^{e,Y}	18.2 ^{d,Y}	1.08 ^{e,Y}	279.5 ^{e,X}	188
	90	357.4 ^{e,X}	11.3 ^{f,Y}	259.1 ^{f,Y}	30.2 ^{f,X}	17.7 ^{d,X}	1.42 ^{f,Y}	283.1 ^{f,X}	195

a, b, c—significant differences between doses of MF; d, e, f—significant differences between doses of AFP; X, Y—significant differences between fertilizers with the same dose; Non—the soil without fertilizer before starting the experiment; MF—mineral fertilizer; AFP—hydrogel capsules with adsorbed P; TP—total phosphorus; AP—available phosphorus; SC—specific conductivity.

Comparing the start of the experiment to the finish, the soil content of all tested metals decreased (Table 4). With increased AFP dose, soil Fe increased. For MF, the opposite was true. The described changes were statistically significant, but not greater than 3.8%. For the smaller doses of fertilizer, a significant effect of the type of fertilizer on soil content of Pb, Cu, Cd, and Zn was found. At 30 kgP/ha, a higher level of metals was found in the MF fertilized soil. For 90 kgP/ha, the metal content was comparable for both types of fertilizer. SC was 252 μS/cm before the experiment and ranged from 185 to 218 afterwards.

Soil pH_{water} increased by 0.1 through the experiment from 7.3 to 7.4. pH_{KCl} was 7.2 at the start and 7.2 to 7.3 at the finish.

4. Discussion

The hypothesis tested in this study was that the AFP alginate preparation with adsorbed P would perform as a fertilizer equally to or better than mineral fertilizer (MF) in

relation to the growth of Italian ryegrass. Overall, the growth results for the two fertilizers were similar. One difference was apparent, however, in that a greater share of germinating seeds was found in the trials fertilized with MF. This may have been caused by the much larger particle size distribution of the AFP fertilizer, resulting in a less even distribution in the soil. Additionally, the AFP cultivated cut I tissue had significantly higher TN content than the MF ones. The main component of AFP, which is alginate, may have contributed to this, increasing the plant's physiological activity and improving the bioavailability of macro and microelements [25]. For both types of fertilizer, the TN content in the subsequent cuts decreased by over 60%. This was caused by the lack of additional N fertilizer during the growing season and it most probably caused the decreased yield observed during the experiment.

The applied fertilizers had a similar effect on the content of the tested forms of soil-P by the end of the experiment. TP and AP had increased to 353 mgTP and 13 mgAP per kgDM in the MF treatment and 361 mgTP and 12 mgAP per kgDM in the AFP treatment. In other studies, AP content was in the range 1–6 mgAP/kgDM from work in subtropical and temperate zones, covering seven cultivation systems and six soil types [43]. The soil-TP content at the end of the experiment was on average seven times higher than the lower limit of soil-TP normally found in soil, which is within the range of 50 to 3000 mgP/kgDM soil [44]. The iron content of the soil was below 700 mg/kg, which characterizes a low level [45]. The content of other, potentially toxic, multivalent metals in the soil was comparable in all trials for both types of fertilization.

The content of toxic metals in the Italian ryegrass tested in our experiment, was comparable to the results from other studies. Darch et al. [46] conducted a pot experiment on the effects of a novel P fertilizer produced from abattoir waste compared to traditional multi-element fertilizer on grass yield in different soil types. The content of metals in grass ranged 1–10 mgCu, 29–743 mgFe and 5–38 mgZn per kgDM, while the average content of Pb and Cd was 11 and 1 mg/kgDM, respectively. A study of the metal content in plants fertilized with mineral fertilizer under field conditions showed that in the case of the meadow sward it amounted to 84 mgFe, 25 mgZn and 6 mgCu per kgDM [47]; higher contents were found in non-fertilized meadow herbs: 240 mgFe, 39 mgZn and 8 mgCu per kgDM [48]. The Italian ryegrass in our experiment had a Cd content three times the concentration permitted in animal feed by the European Commission [49]. This was due to the relatively high ambient Cd level in the soil used in the experiment since the results for both fertilizer types were similar. Our research has shown significantly higher levels of Fe and Cu in the Italian ryegrass fertilized with AFP compared to MF. The levels of these metals were lower than concentrations known to be toxic to plants, namely: >1000 mgFe and 20–100 mgCu per kgDM [46]. The high Cu content indicates the risk of increasing the content of toxic metals in plants fertilized with AFP due to its competitive adsorption to phosphate ions. Municipal wastewater is characterized by a relatively high content of metals, e.g., 0.8 mgCu²⁺, 1 mgZn²⁺ and 0.4 mgPb²⁺ per L [50]. In industrial wastewater, these are even higher, running at 2.1 mgCu²⁺, 17 mgZn²⁺, 6 mgPb²⁺ and 0.1 mgCd²⁺ per L [50].

Alginate is rich in carboxyl, hydroxyl, and other active functional groups, reacting with heavy metals through ion exchange or complex reaction [31]. Studies on the sorption affinity of metals to alginate salts indicated the presence of adsorption of multivalent metals to calcium- [31] and iron-crosslinked alginate adsorbents [35]. The ability of sodium alginate to bind to multivalent cations follows the sequence Pb²⁺ > Cu²⁺ > Cd²⁺ > Ba²⁺ > Sr²⁺ > Ca²⁺ > Co²⁺ > Ni²⁺ > Zn²⁺ > Mn²⁺ [30]. Some ions, e.g., Pb²⁺, Cd²⁺, Cu²⁺, and Zn²⁺ have a higher affinity to alginates than Fe³⁺ [51,52]. The competitiveness of adsorption of various ions in the water phase largely depends on pH [53]. It has been widely reported that pH affects the removal efficiency mainly by changing the surface charge property of the adsorbent. As pH increases, the alginate functional groups de-protonate and the toxic metals uptake capacity significantly increases [54]. The sewage water for which the P adsorption using AF was carried out, came from a small sewage treatment plant located

in an agricultural area in Nowogard (Poland, West Pomeranian Voivodeship). As a result, the concentrations of tested metals (Zn, Cu, Pb, Cd) in the AFP were low and within the threshold limits for fertilizers [55]. Further research is needed to determine the effect of pH and the permissible limit concentrations of multivalent metals in wastewater from which P is recovered using the alginate adsorbent. As with most new alginate adsorbents, the studies here were conducted only in a laboratory setting. Scaling up to real field conditions with varying soil physical and chemical properties, requires further testing of the characteristics and mechanical/thermal stability of the alginate-based preparation in fertilization tests.

Higher amounts of Fe in the Italian ryegrass fertilized with AFP compared to the plants fertilized with MF resulted from the high Fe content in AFP. Fe(III) was the AF hydrogel cross-linking agent, and its content as AFP dry matter was 16.5%. Fe(III) in this form can be quickly released in the event of ion exchange with other multivalent metals or biodegradation of the preparation [35]. The Fe:P ratio calculated for AFP was 0.94, which indicates the high availability of P. The Fe present in the biosolids used for agronomic purposes may reduce the plant-availability of P. Greenhouse studies conducted with a common pasture grass grown in two P-deficient soils amended with 12 biosolids and commercial fertilizer showed that biosolids containing greater than 50 gFe/kgDM were characterized by low plant P availability [56]. P from sewage sludge is more available when the molar ratio Fe:P is less than 1.6. Increasing the Fe:P ratio above this level lowers P-bioavailability, dropping to zero with Fe:P at 9.8 [57].

The comparable yield of the Italian ryegrass obtained using MF and AFP in the pot experiments and similar levels of plant and soil macro and micronutrients confirm that natural and biodegradable alginate-based adsorbents can be an important tool for effective recycling of P. This result is in line with the current EU circular economy vision [3,58], environmental sustainability and green entrepreneurship [59]. The proposed method of P recovery from wastewater treatment products may have a great application potential. TRIZ (Theory of Inventive Problem Solving) identified sewage sludge as a waste with high P recovery potential (up to 90%) [58]. P recovery can be more sustainable based on the circular economy 4Rs (reduction, recovery, reuse, and recycling). As long as efficient and advanced wastewater treatment techniques are an essential part of water bodies protection, the produced sewage sludge will be a significant source of P. Much of the limitations associated with fertilizing soils with sewage sludge can be eliminated by binding P onto alginate beads. The most burdensome limitations include the dispersion of metals and pathogens in the environment and the introduction of excessive amounts of agronomically inaccessible forms of P [1], which, in the process of soil erosion, get into surface waters, contributing to accelerated eutrophication. This considerable risk results from the fact that the concentration of P in soil solution necessary for proper development of plants (0.2–0.3 mgP/L) is more than ten times the concentration of P in water limiting the development of algae (0.02 mgP/L) [60].

The innovative strength of the proposed solution is a waste-free use practically at full volume of the adsorbent enriched with P. Therefore, this novel method based on alginate adsorbents could be cost-effective at large-scale commercial scale. More common application of this type of method and financing for its development remain limited. Legislation relating to the management of P is mainly associated with its potential to pollute natural ecosystems. Little or no regulations promote the recovery of P from wastewater into forms suitable for use as fertilizer [2,3].

5. Conclusions

MF and AFP fertilization produced similar crop yields of Italian ryegrass and had similar plant and soil macro- and micro-element chemical composition. However, crops under AFP had higher content levels of Fe and Cu. Therefore, we recommend further work to (a) determine the safe concentration limits of multivalent metals from the wastewater where P is recovered, (b) test the mechanical/thermal stability of the alginate fertilizer and

(c) carry out longer-term field-scale trials to test agronomic efficiency. Alginate fertilizer activated with iron and enriched with P from wastewater has the potential to improve concentrations of essential elements in crops while maintaining good yields. This is in line with the EU circular economy vision.

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