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Post-Recycling Sodium Polyacrylate with Nanostructural Halloysite Additive as the Basic Components of the New Hybrid Soil Modifier—The Circular Economy Rules for SAP in Agriculture

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Abstract: Post-recycling sodium polyacrylate (SPA) derived from the selective recycling of personal hygiene products was tested as a potential key component of soil modifiers. Recycled SPA in combination with layered aluminosilicate (halloysite) with the sorption capacity of fertilizers allows for the creation of a fully functional, original system responsible for both water retention in soil and controlled dosing of fertilizers. The use of post-recycling SPA (possibly partially supplemented with virgin SPA) is advantageous for the natural environment. The results of different water types retention in post-recycling SPA (deionized water, rainwater, tap water) are discussed. The most beneficial effects of R-SPA swelling and water accumulation are achieved when it comes into contact with rainwater. The clear impact of Mg^{2+} ions on the sorption capacity of R-SPA introduces the need for a technological compromise between the solution composition (N, P, K or N, P, K, Mg) affecting its fertilization value and the possibility of obtaining maximum R-SPA swelling. The sorption capacity of R-SPA can be slightly increased by using R-SPA/V-SPA mixtures, but R-SPA still plays a decisive role in this system. The possibility of technological adjustment of the leaching rate of fertilizer components under dynamic conditions using different combinations of (R-SPA/V-SPA)/HAL was demonstrated by column tests.

Keywords: post-recycling sodium polyacrylate; halloysite; slow releasing fertilizer; water retention; hybrid soil modifier

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Citation: Sakiewicz, P.; Piotrowski, K.; Rajca, M.; Cieślak, S. Post-Recycling Sodium Polyacrylate with Nanostructural Halloysite Additive as the Basic Components of the New Hybrid Soil Modifier—The Circular Economy Rules for SAP in Agriculture. *Resources* **2024**, *13*, 75. https://doi.org/10.3390/resources13060075

Academic Editor: Benjamin McLellan

Received: 15 April 2024
Revised: 27 May 2024
Accepted: 28 May 2024
Published: 31 May 2024

1. Introduction

Superabsorbent polymers (SAP) represent a special, relatively large group of polymeric materials, mainly characterized by a unique natural ability to absorb and retain relatively large volumes of water or aqueous solutions [1]. The most common representative of this group on the market is sodium polyacrylate (SPA). This particular property (high water absorption capacity) is very desirable in the case of disposable hygiene products (absorbent hygiene products, AHPs) whose effectiveness is based on the high absorbancy of physiological fluids [2]. The basic active ingredient in AHPs is sodium polyacrylate, a sodium salt of polyacrylic acid [$–CH_2–CH(CO_2Na)–]_n$ [3]. It is also widely used in agriculture. High absorption ability results from the specific three-dimensional polymer network structures that, when in contact with water, do not dissolve but undergo spatially significant swelling [1]. An additional advantage is its inert impact on the natural environment—after its assumed period of operation, it decomposes into non-toxic substances and undergoes gradual mineralization. There are also other superabsorbents, both natural (e.g., based on cellulose [4]) and synthetic (e.g., based on acrylate [4]), where the synthesis conditions can be modified to produce the desired higher performance and durability [1]. In particular, these are desirable synthesis products of hydrophilic characteristics, being non-toxic compounds, of biosphere-friendly biodegradation, partial mineralization, and biocompatibility [5]. Such properties are related to target applications, especially in: AHPs, agriculture, forestry, horticulture with the possibility of effective bioremediation, industrial automation with innovative biosensors, applications in thermal energy storage, in the pharmaceutical and food industries [1], in separation systems as fiber and textile components, nanocomposite materials [6], for specialized applications in construction, and others [7,8]. These are also applied in medicine for controlled and point dosing of drugs.

An example of the use of superabsorbent polymers may be ground-cement subsurface insulations with self-healing [9], demanding in terms of permeability and retention (sorption effect). Other studies have shown the high absorption capacity of ions in water by these structures [10], which indicates the possibility of their use for soluble salt retention.

Due to their unique sorption and water retention capabilities, superabsorbents can be used in agriculture [4]. The main expectations of this material introduced into soil are the possibility of water retention and dissolved nutrients [11]. The cycles of sorption and desorption have a positive effect on increasing the soil porosity [11,12] (reducing bulk density), increasing the possibilities of water retention in the soil, stabilizing, and cyclic renewal of spatial distribution channels, in particular in the rhizosphere, directly increasing the effects in agriculture (e.g., tested SAP dose 60–90 kg ha^{-1} in potato cultivation [11]). The possibility of water retention, spatial micro-distribution of the nutrients, and their slow release into the rhizosphere allows to increase the efficiency of agricultural, fruit, and forest crops in regions with a dry climate [13], and ecological renovation of land intensively used for industrial purposes, like in mining areas [10] (accumulation and concentration of soluble salts). It enables at least partial independence from the climate, in particular from atmospheric precipitation, thus slowing the controlled dosing of fertilizers, increasing the efficiency of their target use, and reducing losses (eutrophication prevention) [13].

For example, ref. [14] presents a proposal to integrate the biodegradable polymer polycaprolactone (PCL) of hydrophobic properties with guar gum (GG) responsible for the swelling and with halloysite nanotubes (HNTs) as a natural filler for slow release of nutrients. This encapsulation method was tested on selected nitrogen and phosphorus compounds, showing improved dispensing over uncoated materials [14].

The literature also shows that cheap aluminosilicate materials, for example, nanostructural halloysite, bentonite, and kaolinite (smectites), are increasingly used as natural functional fillers, e.g., in agriculture [15]. The work [16] presents the use of halloysite nanotubes (HNTs) for the sorption of phosphates(V) from uncontrolled leachate derived from agricultural lands. The possibility of adsorption for HNTs in the powder form (79.5%) and dosed in a granular form (94.7%) [16] was demonstrated. The HNTs show heterogeneity resulting from both the porous structure and the surface morphology, as well as the presence of specific functional groups [16]. Another work demonstrated promising application trends related to the modification of HNTs with iron oxide (Fe_2O_3) in the nanoscale, which increases the adsorption capacity of oxide surfaces responsible for the sorption of phosphates(V) using the ligand exchange mechanism and the mechanism of internal sphere complex formation [17]. The influence of Fe_2O_3 concentration, adsorbent dose and pH, interphase contact time, the initial concentration of phosphates(V), and other ions on the efficiency of phosphates(V) adsorption was verified experimentally [17]. The importance of pH for the efficiency of phosphates(V) adsorption on halloysite was also confirmed in [18], whereas in [19], the alternative possibilities of using vermiculite were indicated.

Biodegradable polymers synthesized from poly(hydroxybutyrate) (PHB) and used in the slow, controlled dosing of nitrogen compounds were presented in [5], where the relationships between the polymer characteristics and the kinetics of the release of the sorbed compounds were studied, mainly by correlation with the rate of PHB biodegradation [5].

Two ways of contacting NPK fertilizers have been experimentally verified—by direct mixing with a polymer and by dispersing the NPK compounds onto bentonite and then mixing it with the polymer [5]. Advantageous, slow release of NPK substances, in comparison with direct dosing of NPK solutions into the biosphere, was confirmed. The use of bentonite made significantly extending the time of controlled dosing of fertilizers (4–11% after 240 h, while the simpler PHB/NPK system—up to 37%) possible [5].

In general, attention should be focused on the complexity of the sorption process mechanism itself, combining both surface adsorption and the absorption process in the entire volume, which is directly related to the absorption of solutions of different chemical compositions. The chemical composition of the solution also significantly influences the volumetric absorption capacity due to the interaction of its compounds with the chemical structure of the polymer (in particular, pH plays a key role). These factors also potentially cause some changes in the spatial structures of superabsorbents, modifying with time (with an increasing number of sorption and desorption cycles) the possibility of the accumulation of water or aqueous solutions. The research [20] clearly indicated the importance of the quality of the water used (distilled water, tap water, extracts of compounds from the given soil). The number of subsequent sorption-desorption cycles was also of key importance. The research [20] showed that after 5 absorption/desorption cycles, the possibility of absorbing doses of tap water, extracts of soil substances in distilled water, and extracts of soil substances in tap water decreased by 73.4–99.3% in relation to the distilled water. The chemical composition of water has been found to have a great influence on the so-called primary water absorption. The possibilities of absorption, thus water retention, clearly increased with increasing superabsorbent concentration. However, with repeated use, these generally decreased [20]. The studies showed no significant changes in the repeatable water absorption at different temperatures (50, 25, and −4 °C) [20]. Maintaining the hydrophilic capacity of the superabsorbent even for a longer time was noted, with the degree of drying of the hydrogel systems not exceeding 80%. The process efficiency during repeated use depended primarily on the stability of the absorption process, the structural properties of the gel, the superabsorbent concentration, the chemical composition of the water, and soil moisture [20].

The complexity of the polymer-sorbed substance system, its chemical composition, pH, and multiplicity of use indicate that the net effect is so complex that it is practically impossible to predict it theoretically. Thus, a series of experiments identifying the conditions of multiple cyclic sorption and desorption under different operating conditions should be conducted.

Based on the available literature data, the current main directions of recycling disposable hygiene materials with the addition of superabsorbents can be determined as technological conversions of a separated fraction of biodegradable materials (composting, methane fermentation) and fractions of recoverable plastics.

The possibility of using superabsorbent from recycling recovery, taking into account its very large material flows on a global scale [21,22], is also important. This method of using recovered superabsorbent from disposable hygiene products establishes certain possibilities for its reuse in the second (and possibly subsequent) product life cycle(s), which can significantly reduce current environmental problems related to its safe disposal [23–25]. Due to the possible permanent changes in the polymer network, directly responsible for the possibility of water retention in cyclic sorption-desorption, directed technological research is important to determine the practical limitations in the use of recovered, post-recycling superabsorbent—in particular for the accumulation and slowed release of various nutrients from multi-component aqueous solutions. This may be important for determining the suitability of this irrigation/fertilization technology in agriculture, forestry, and horticulture. Only available in [26], some reports can be found on the experimental use of reclaimed sodium polyacrylate hydrogel obtained from used diapers based on distilled water for evaluating swelling and deswelling dynamics and water retention capability (effects of salt density, temperature, and pH). Numerous current literature reports related to the use of superabsorbent polymers in agriculture [27–49] prove that the discussed topic is important both in terms of sustainable development guidelines and the Circular Economy strategy.

The practical lack of available information on the use of post-consumer SPA fractions in agriculture, along with available statistical data on their accumulation on a global scale, inspired the authors to undertake as comprehensive technological research in this promising, unexplored direction as possible.

The main goal of the presented research was to experimentally verify—in a systematic manner—the possibility of innovative use of recycled sodium polyacrylate as the main component of the original multifunctional (water retention, sorption, fertilizing) hybrid soil modifier responsible for the possibly controlled water flux in the rhizosphere. The introduction of this type of cheap and environmentally friendly additive will both increase the efficiency of agricultural crops and help solve the problem of the utilization of material fractions of used disposable hygiene products.

2. Materials and Methods

To carry out the research, both virgin sodium polyacrylate, V-SPA (HRT Company, Kołobrzeg, Poland, size fraction 0.1–1 mm) and post-consumer recycled sodium polyacrylate (R-SPA) were used. The R-SPA was the polymer fraction recovered from AHPs (mainly from disposable diapers and pampers for children and adults). Sodium polyacrylate obtained through the mechanical recovery was hygienized (elimination of microorganisms, viruses, bacteria, etc.) and dried in accordance with the procedure developed in the project (as confidential, it constitutes the company know-how of "TAMAX" Ltd., Sędziszów, Poland). Its fraction also contained natural and biodegradable cellulose fibers, which, due to their structure and mixing, could not be separated. The R-SPA came from diapers separated and donated by residents in the selective collection process carried out in the Świętokrzyskie, Małopolskie, and Silesian voivodeships (southern Poland region). A large part of the analyzed material also included diapers for seniors collected selectively in social welfare homes for the elderly. It should be emphasized that the disposable hygiene materials tested were a review profile of AHPs available on the market, which was aimed primarily at practical verification of the process capabilities of the presented recycling technology.

Halloysite (Figure 1) (HAL) is an aluminosilicate clay from the kaolinite subgroup. As a mineral used in the research, it was derived from the Polish Lower Silesia Dunino Deposit. This geological deposit is characterized by a specific structure and chemical composition, resulting in unique properties. Micro- and nano-structural SEM analysis revealed that the halloysite samples consisted of mixed nanotubes (HNTs) [50] and nanoplatelets (HNPs). Elemental chemical analyses were conducted for 5 dried raw samples, and the averaged concentrations of the major elements (energy-dispersive X-ray spectroscopy (EDS)) analysis (as mass %) were: O (43.39%), Si (19.51%), Al (18.71%), Fe (12.92%), and Ti (1.42%) [51]. The X-ray diffraction of this material revealed the following minerals: halloysite, kaolinite, hematite, magnetite, quartz, magnesioferrite, rutile, ilmenite, geikielite, goyazite, gorceixite, and crandallite.

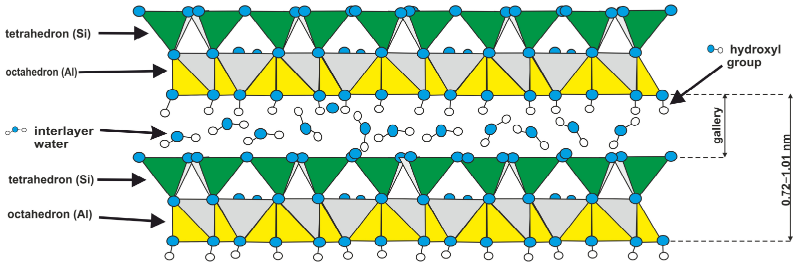


Figure 1. Halloysite (HAL) single crystal structure.

2.1. Water Absorption Tests for V-SPA/R-SPA

Three different water types (different sources in practical technological applications) were used in research to test the differentiated behavior of "V-SPA/R-SPA—water" systems.

The influence of the chemical composition of the solvent—water, especially for more complex solutions—on the absorption capacity of superabsorbents was mentioned in [52]. The following three water types were selected as the most representative:

1. Deionized water—as a reference, representing pure water without any concurrent ions and other dissolved chemicals (apparatus System Elix® Advantage, Merck Millipore, Burlington, MA, USA (resistivity > 5 MΩ cm (25 °C), TOC < 30 ppb with Vent Filter MPK01 by Merck Millipore, Guyancourt, France));
2. Rainwater—natural atmospheric rainfall of typical chemical composition;
3. Tap water—typical water from the municipal network, used for artificial irrigation of urban green in built-up areas.

The concept of the described technical solution assumes that in the natural environment, if it is used as a hybrid soil modifier, resorption and desorption processes will occur mainly with rainwater.

2.2. Tests of Saturation of the V-SPA/R-SPA Mixtures with Raw Nanostructural Halloysite with Aqueous Solutions

In the second set of tests, experimental verification of the influence of the proportion of various components of the hybrid soli modifier prototype was carried out. The V-SPA/R-SPA mixtures and adsorbent represented by halloysite (raw) were exposed under controlled conditions to direct contact with aqueous solutions of different chemical compositions (thus V-SPA/R-SPA swelling). The aforementioned solutions were:

- Rainwater;
- Aqueous solution representing N, P, and K ions (based on deionized water);
- Aqueous solution representing N, P, K, and Mg ions (based on deionized water).

The mass of V-SPA, R-SPA, and halloysite samples was measured using an analytical laboratory balance, the Sartorius MC1 analytical AC 210 S, Goettingen Germany, with an accuracy of ±0.0001 g. Laboratory dryer FD-S 056 by BINDER GmbH, Tuttlingen, Germany, and the temperature of the drying process at 50 °C with air circulation were applied.

The details of combinations of the analyzed systems used (proportions)—with the codes 1A–3C—are presented in Table 1.

Table 1. The analyzed systems used in the tests. (Reference solutions of 1000 mg/dm^3 were used).

Code	Solid Mixture Composition	Absorption Mixture Composition
1A	5.812 g R-SPA + 125.7942 g raw HAL	50 mL NO_3^- + 50 mL PO_4^{3-} (with K^+ ions) + 900 mL deionised water
1B	5.812 g R-SPA + 125.7942 g raw HAL	50 mL PO_4^{3-} (with K^+ ions) + 50 mL Mg^{2+} (with NO_3^- ions) + 900 mL deionised water
1C	5.812 g R-SPA + 125.7942 g raw HAL	rainwater
2A	5.8372 g V-SPA + 124.0747 g raw HAL	50 mL NO_3^- + 50 mL PO_4^{3-} (with K^+ ions) + 900 mL deionised water
2B	5.8372 g V-SPA + 124.0747 g raw HAL	50 mL PO_4^{3-} (with K^+ ions) + 50 mL Mg^{2+} (with NO_3^- ions) + 900 mL deionised water
2C	5.8372 g V-SPA + 124.0747 g raw HAL	rainwater

Table 1. *Cont.*

Code	Solid Mixture Composition	Absorption Mixture Composition
3A	2.6235 g R-SPA + 2.5203 g V-SPA + 125.4919 g raw HAL	50 mL NO_3^- + 50 mL PO_4^{3-} (with K^+ ions) + 900 mL deionised water
3B	2.6235 g R-SPA + 2.5203 g V-SPA + 125.4919 g raw HAL	50 mL PO_4^{3-} (with K^+ ions) + 50 mL Mg^{2+} (with NO_3^- ions) + 900 mL deionised water
3C	2.6235 g R-SPA + 2.5203 g V-SPA + 125.4919 g raw HAL	rainwater

For each individual test, from 0.4908 g up to 0.7834 g of the solid mixture was taken and contacted with the solution. Then the excess volume of the solution (after visually determining the state of complete saturation of the solid system) from the laboratory glass was carefully removed manually with the use of special filter paper.

2.3. Column Tests (Dynamic Leaching of Nutrients from the Prototype Hybrid Soil Modifier)

The simulation of conditions for the complex cyclic process of leaching (extraction)/resorption of nutrients resulting from the infiltration of atmospheric precipitation waters (or the alternative use of artificial irrigation) was carried out using the column tests.

Various compositions of solid mixtures were used. Solid materials in the form of powders were introduced into glass laboratory columns in special sleeves made of material permeable to the inlet solution and the filtrate (extract). Each powder was poured into 100 mL of an aqueous solution of N, P, and K (optionally Mg). After 24 h of contact (it is assumed to obtain a practical sorption equilibrium from the point of view of the production technology of hybrid soil modifier), excess N, P, and K (optionally Mg) solutions were collected from the bottom of the column.

The details are presented in Table 2.

Table 2. The details of column tests (dynamic leaching of nutrients from the prototype hybrid soil modifier). Reference solutions of 1000 mg/dm^3 were used.

	Solid Mixture Composition	Total Solid Mass, g	Aqueous Mixture Composition	Excess Solution, mL
Column 1	R-SPA + raw HAL 1: 23 ± 5%	13.1844	50 mL NO_3^- + 50 mL PO_4^{3-} (with K^+ ions) + 900 mL deionised water	50.5
Column 2	V-SPA + raw HAL 1: 23 ± 5%	13.1414	50 mL NO_3^- + 50 mL PO_4^{3-} (with K^+ ions) + 900 mL deionised water	10.5
Column 3	R-SPA + V-SPA + raw HAL 1:1: 23 ± 5%	13.0014	50 mL NO_3^- + 50 mL PO_4^{3-} (with K^+ ions) + 900 mL deionised water	29.0
Column 4	R-SPA + raw HAL 1: 23 ± 5%	13.1139	50 mL PO_4^{3-} (with K^+ ions) + 50 mL Mg^{2+} (with NO_3^- ions) + 900 mL deionised water	80.0
Column 5	V-SPA + raw HAL 1: 23 ± 5%	13.0495	50 mL PO_4^{3-} (with K^+ ions) + 50 mL Mg^{2+} (with NO_3^- ions) + 900 mL deionised water	60.0
Column 6	R-SPA + V-SPA + raw HAL 1:1: 23 ± 5%	13.0981	50 mL PO_4^{3-} (with K^+ ions) + 50 mL Mg^{2+} (with NO_3^- ions) + 900 mL deionised water	74.0

Saturating solutions were prepared by adding to deionized water a specified volume of the standard solutions of NO_3^- (Merck, No. 09713), K^+ (Merck, No. 00615), PO_4^{3-} (HACH, LCK350), and Mg^{2+} (HACH, LCK326) ions. Ion identification in the saturating solution samples was performed using Merck and HACH reagents (NO_3^-, K^+) and cuvette (PO_4^{3-}, Mg^{2+}) tests; the results are presented in Table 3.

Table 3. The results (mean values) of chemical analyses of the composition of aqueous saturating solutions used in the column tests.

Solution of:	NO_3^- mg/dm^3	PO_4^{3-} mg/dm^3	K^+ mg/dm^3	Mg^{2+} mg/dm^3
N, P, K	65.1	50.73	33.7	0
N, P, K, Mg	1708	57.5	29.7	50.7

The readings of the identified ions were made with the Spectroquant Pharo 100 spectrophotometer by Merck, Darmstadt, Germany (NO_3^-, K^+ ions) and the spectrophotometer DR 5000 by HACH LANGE GmbH (Berlin, Germany) (PO_4^{3-}, Mg^{2+} ions).

After the saturation of the (V-SPA/R-SPA)/HAL solid bed with appropriate nutrients, the leaching tests were conducted. For the experimental simulation, the actual average amount of atmospheric precipitation per 1 m^2 of 694 dm^3 recorded at the Kielce-Suków (Poland) measuring station in 2019 was assumed for the simulation of real agricultural conditions. It simulated the total volume of the leaching agent naturally infiltrating through the investigated system. Based on this, the time distribution (slow release effect) of the concentration of nutrients in the eluate was determined analytically. The appropriate filtrate (extract) volumes were collected as follows:

- Test reception No 1: 20 mL to be rejected;
- Test reception No 2: 10 mL collected for analysis;
- Test reception No 3: 20 mL to be rejected;
- Test reception No 4: 10 mL collected for analysis.

Preliminary observations of the (V-SPA/R-SPA)/HAL systems were carried out using light (optical) microscopy. It enabled the initial selection of surface areas of samples for more thorough observational studies using Zeiss Supra 35 scanning electron microscopy (SEM) with a chemical and phase composition analysis system—the Thermo Scientific™ EDX UltraDry EDS spectrometer (the laboratory of the Faculty of Mechanical Engineering of the Silesian University of Technology in Gliwice). To better render surface details, some samples were sputtered in a BAL-TEC SCD 050 sputter coater. Energy-scattered X-ray spectroscopy (EDS) enabled the analysis of the chemical composition both in the micro-areas of the tested samples as well as the analysis of the 2D distribution of the investigated elements in relatively larger areas. An analysis of the structure of the surface coverage of SPA by halloysite particles was carried out. The spatial structure of (V-SPA/R-SPA)/HAL was also analyzed in the destination environment—in the sample of soil—and the elemental composition of the tested system was verified based on EDS area analysis.

3. Results and Discussion

3.1. Water Absorption Tests

On the basis of measurement data, the technological behavior of the R-SPA-water system was determined. The results of R-SPA saturation with water of various types are shown in Table 4.

On the basis of the data presented in Table 4, it is clearly visible that in the case of deionized water, formally representing "chemically pure water", the water-saturated sample mass was 81 times higher compared to the mass of the dry R-SPA sample. This is a relatively high value considering its future sorption use as a water reservoir for the root systems of the crops.

Table 4. The results of R-SPA saturation with water of various types.

Water Type	Mass of the Dry R-SPA Sample [g] A	Mass of Water-Saturated R-SPA Sample [g] B	Increase in the Initial R-SPA Sample Mass in Effect of Saturation B/A
Deionized water	1.5356	124.4536	81.0
Rainwater	1.3006	110.7946	85.2
Tap water	1.2136	83.5430	68.8

It should also be noted, that in the case of rainwater, even slightly greater (more than 85-fold) increase in the mass of dry R-SAP after its direct contact with rainwater was obtained. This suggests both a favorable chemical composition and potential advantageous proportions of individual chemical compounds dissolved in natural rainwater, increasing the sorption capacity of this system.

In the case of tap water, a significantly lower, about 69-fold increase in the mass of water-saturated R-SPA was observed. This clearly proves the lower technological value of tap water for the purpose of its accumulation and sorption by R-SPA, which is to be the main component of the original hybrid soil modifier. In such agricultural conditions, with the absolute necessity of using tap water from the municipal network for cultivation, it will be suggested to:

- Mix tap water with rainwater;
- Use an increased addition (proportion) of V-SPA to the original hybrid soil modifier;
- Increase the proportion of R-SPA in relation to other components of the original soil modifier;
- Modify the chemical composition of tap water immediately before introducing it to agricultural crops or urban green areas (application of a technological buffer correcting the composition of the tap water with the use of some cheap, environmentally neutral chemicals that can be commonly used on a mass scale).

Based on these data, it is possible to suggest more favorable watering conditions with rainwater (for example, natural cyclic watering based on atmospheric precipitation and rainwater accumulation systems, irrigation systems distributing this rainwater, etc.) than with water from the water distribution network due to the different chemical composition of both water types. This is important, for example, in greenhouse crops where it may not be possible to come into direct contact with rainfall but where rainwater is more beneficial than tap water.

It is also clearly visible that the presence of other chemical compounds (dissolved ones, absorbed gases, ions) does not only adversely affect the ability of water accumulation in R-SPA, as quantified by the multiplicity of the increase in its mass associated with sorption (as in the case of directly applied tap water), but it can also be advantageous—as is the case with rainwater. Hence, the key issue is the correct, rational selection (addition, removal, pH correction) of these components, their concentrations, and proportions for the optimal use of R-SPA in the agricultural area.

An important technical issue is also the dynamics of the stored water release (desorption) from the swollen R-SPA (Table 5). A natural release mechanism of water in the form of natural drying in contact with ambient air (natural convection) at room temperature was applied.

As a result of another test related to drying in the conditions of natural atmospheric air convection, a similar behavior in terms of the dynamics of desorption of deionized water and rainwater is clearly visible. In the assumed periods of verification of the R-SPA mass (after 3, 10, and 35 days), almost identical mass losses were observed, presented here as % of the initial mass: 88.97% (deionized water) and 89.36% (rainwater), 55.30% and 53.91%, as well as 10.45% and 11.36%, respectively.

Table 5. The desorption tests from R-SPA—dynamics of the accumulated water release.

Water Type	Mass of the Dry R-SPA Sample [g]	Mass of the Saturated R-SPA Sample [g]	Mass of the R-SPA Sample after 3 Days of Desorption [g]	Mass of the R-SPA Sample after 10 Days of Desorption [g]	Mass of the R-SPA Sample after 35 Days of Desorption [g]
Deionized water	1.5356	124.4536	109.3103	63.0569	1.4666
Rainwater	1.3006	110.7946	97.6468	53.8527	1.2783
Tap water	1.2136	83.5430	67.4653	29.5454	0.9827

However, in the case of tap water (from the municipal network), faster desorption was observed in the first two test points—86.97% (compared to the previous ones at the level of 88.97–89.36%) and 46.05% (at the level of 53.91–55.30%). This, however, significantly slows down at the end of the drying process, where it reached 15.23% at the last measuring point (compared to the previous ones at the level of 10.45–11.36%).

The observed different dynamics of water release from the R-SPA for different chemical compositions of water must be taken into account when analyzing the target application of the original hybrid soil modifier for the planning of irrigation periods or its cyclic replacement (supplementation).

3.2. Tests of Saturation of the V-SPA/R-SPA Mixture with Raw Halloysite with Aqueous Solutions of Different Chemical Compositions

The experimental data corresponding to the saturation tests of the V-SPA/R-SPA mixtures with raw nanostructural halloysite and aqueous solutions of different chemical compositions are presented in Table 6.

Table 6. The results of saturation tests of V-SPA/R-SPA mixtures with raw nanostructural halloysite with aqueous solutions of different chemical compositions.

Sample Code *	Mass of Dry Sample [g] A	Mass of Saturated Sample [g] B	Relative Mass Gain after Saturation B/A	Mass of Sample after 4 Days of Solution Release [g]
1A	0.7834	5.7774	7.37	0.7608
1B	0.4908	1.6629	3.39	0.4818
1C	0.5138	5.5663	10.83	0.5001
2A	0.5333	8.5618	16.05	0.5288
2B	0.5063	1.9253	3.80	0.4973
2C	0.5265	13.3049	25.27	0.5234
3A	0.5719	5.5972	9.79	0.5681
3B	0.5193	1.3082	2.52	0.5029
3C	0.5282	6.9786	13.21	0.5267

* Sample code—see Table 1.

On the basis of the measurement data (Table 6), it can be concluded that in the case of a system with R-SPA enriched with raw nanostructural halloysite, the largest mass gain (about 11 times), indicating the intensification of the sorption process, is obtained upon contact with rainwater, which may come from natural atmospheric precipitation (its potential favorable composition and proportions of chemicals were also noted in the previous section).

In the case of an aqueous solution of N, P, and K contacted with the solid mixture during impregnation, a much smaller increase (7.37 times) of the mass was observed, which proved the inhibitory effect of N, P, and K components on the sorption, affecting its resulting saturation (sample 1A).

The lowest value of the mass increase (3.39 times—sample 1B) was observed for the N, P, K, and Mg systems, which proves the possible selective inhibitory effect of, first of all, the additional component—Mg^{2+} ions. The clear influence of Mg^{2+} ions on a significant limitation of the capacity in relation to the aqueous solution of N, P, K, and Mg proves the need to look for a compromise—the technologically optimal qualitative and quantitative dose of fertilizer ingredients (N, P, K or N, P, K, Mg) in relation to both the fertilization value of the soaking solution as well as its mass capable of the maximum swelling of the SPA.

The replacement of R-SPA with V-SPA shows the possibility of a significant increase in sorption capacity. Therefore, the possibility of producing an original hybrid soil modifier with some fraction of V-SPA should also be technologically considered in the case of the non-availability of R-SPA.

In the case of rainwater, an over 25-fold increase in mass was observed, compared to an 11-fold increase in mass only corresponding to the use of R-SPA. It is a significant increase, mainly related to the properties of a new V-SPA not yet recycled, along with all physical and thermal operations related to its purification, separation, etc., having a complex effect on the structure of the substance (polymer history) directly determining its sorption abilities.

In the case of replacing rainwater with an aqueous solution of N, P, and K, an over 16-fold increase in the mass of the system after sorption was identified. It, compared to R-SPA (7.37-fold), represents a noticeable, favorable, over-two-fold increase.

On the other hand, in the case of using an aqueous solution of N, P, K, and Mg, only ca. 3.8-fold increase in the mass of the sorption system was observed, that in comparison to R-SPA (3.39-fold increase in mass), is an almost identical result. Thus, in the case of an aqueous solution of N, P, K, and Mg, the use of V-SPA and R-SPA is, from a technological point of view, associated with the same anticipated effect.

The use of a V-SPA and R-SPA mixture (more or less 50% each) with a practically unchanged dose of raw halloysite leads to intermediate results. Nevertheless, there is a clearly noticeable tendency to approach with an intermediate result the effect obtained with the use of R-SPA. This proves that introducing the V-SPA to the system by mixing it with the R-SPA does not lead to a proportional improvement in the sorption properties of the system. It also proves the process-dominant role of R-SPA.

In the case of rainwater, a 13.2-fold increase in the mass of the system was achieved, which is—despite the use of practically equal parts of V-SPA and R-SPA—a result clearly similar to the effect (10.83-fold increase in mass) reflecting the use of R-SPA than when using V-SPA (25.27-fold increase in mass).

Similarly, when using an aqueous solution of N, P, and K, the obtained mass increase (9.79-fold increase) is similar to the effect observed for R-SPA (7.37-fold increase) in the case of V-SPA (16.05-fold increase).

In the case of using an aqueous solution of N, P, K, and Mg, only a 2.52-fold increase in the mass of the system was observed, which is the lowest result observed for this system during all nine tests (Table 6).

From a technological point of view, a recommendation can be for the use of R-SPA (because the admixture of V-SPA does not cause a significant increase in the sorption capacity of the SPA mixture) or a completely new V-SPA, which gives a clear increase in the sorption effectiveness. The technological decision on the chemical composition of the original hybrid soil modifier should take into account all agricultural market conditions and economic conditions of the irrigation, fertilizing, and sorption aspects.

3.3. Column Tests (Dynamic Leaching of Nutrients from the Prototype Hybrid Soil Modifier)

The results of chemical analyses obtained for the aqueous N, P, K and N, P, K, Mg saturating solutions and the simulated dynamic leaching of nutrients from such constructed prototypes of hybrid soil modifiers are presented in Table 7.

Table 7. The results of chemical analyses—the dynamic leaching of nutrients from the prototypes of hybrid soil modifiers.

Ion Type	**In Excess Solution in the Column**				**Test Reception No 2 ***				**Test Reception No 4 ***			
Column 1												
	Test 1	Test 2	Test 3	Mean	Test 1	Test 2	Test 3	Mean	Test 1	Test 2	Test 3	Mean
NO_3^- mg/dm^3	73.8	73.6	73.7	73.7	25.8	25.7	25.8	25.76	21.4	21.5	21.5	21.46
PO_4^{3-} mg/dm^3	35.3	35.4	35.2	35.3	0	0	0	0	13.6	13.6	13.6	13.6
K^+ mg/dm^3	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30
Column 2												
	Test 1	Test 2	Test 3	Mean	Test 1	Test 2	Test 3	Mean	Test 1	Test 2	Test 3	Mean
NO_3^- mg/dm^3	68.3	68.4	68.4	68.36	30.8	30.9	30.9	30.86	21.0	21.3	20.9	21.1
PO_4^{3-} mg/dm^3	32.5	32.6	32.6	32.56	0	0	0	0	0	0	0	0
K^+ mg/dm^3	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30
Column 3												
	Test 1	Test 2	Test 3	Mean	Test 1	Test 2	Test 3	Mean	Test 1	Test 2	Test 3	Mean
NO_3^- mg/dm^3	69.9	69.9	70.1	69.96	28.9	28.9	28.9	28.9	22.4	22.3	22.4	22.36
PO_4^{3-} mg/dm^3	27.4	27.4	27.4	27.4	8.63	8.64	8.64	8.63	7.52	7.56	7.53	7.54
K^+ mg/dm^3	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30
Column 4												
	Test 1	Test 2	Test 3	Mean	Test 1	Test 2	Test 3	Mean	Test 1	Test 2	Test 3	Mean
NO_3^- mg/dm^3	1570	1570	1568	1569.3	376	378	378	377.3	304	304	308	305.3
PO_4^{3-} mg/dm^3	32.2	32.2	32.2	32.2	6.34	6.34	6.36	6.35	2.09	2.12	2.14	2.12
K^+ mg/dm^3	43	44	44	43.7	<30	<30	<30	<30	<30	<30	<30	<30
Mg^{2+} mg/dm^3	44.7	44.7	44.7	44.7	1.36	1.36	1.36	1.36	0.649	0.649	0.649	0.649
Column 5												
	Test 1	Test 2	Test 3	Mean	Test 1	Test 2	Test 3	Mean	Test 1	Test 2	Test 3	Mean
NO_3^- mg/dm^3	1720	1714	1714	1716	534	538	542	538	426	426	424	425.3
PO_4^{3-} mg/dm^3	24.5	24.6	24.5	24.53	0	0	0	0	1.69	1.72	1.73	1.71
K^+ mg/dm^3	25	25	26	25.3	<30	<30	<30	<30	<30	<30	<30	<30
Mg^{2+} mg/dm^3	30.4	30.4	30.4	30.4	0.569	0.569	0.569	0.569	0.028	0.028	0.028	0.028
Column 6												
	Test 1	Test 2	Test 3	Mean	Test 1	Test 2	Test 3	Mean	Test 1	Test 2	Test 3	Mean
NO_3^- mg/dm^3	1522	1516	1518	1518.7	444	448	448	446.7	292	278	232	267.3
PO_4^{3-} mg/dm^3	0	0	0	0	1.21	1.48	1.57	1.42	1.07	1.22	1.32	1.20
K^+ mg/dm^3	31	31	31	31	<30	<30	<30	<30	<30	<30	<30	<30
Mg^{2+} mg/dm^3	41.1	41.1	41.1	41.1	1.9	1.9	1.9	1.9	0	0	0	0

* The appropriate filtrate (extract) volumes were collected in the following test schedule: (1) test reception No. 1: 20 mL to be rejected; (2) test reception No. 2: 10 mL collected for chemical analysis; (3) test reception No. 3: 20 mL to be rejected; and (4) test reception No. 4: 10 mL collected for chemical analysis.

When analyzing the results presented in Table 7, significant sorption effects of potassium ions and phosphate(V) ions can be noticed (chemical analysis of the composition of the excess solution drained from the columns after obtaining the state of practical sorption equilibrium in multicomponent solutions—mass balance calculations).

Systematic analysis of the composition of the eluting solutions (rainwater introduced at the top of the column simulating the contact of the original hybrid soil modifier with natural rainfall, in the unit surface amount specified for a given geographical location, amounting to 694 dm^3/m^2) indicates a significant sorption effect of potassium ions, but also the lack of possibility or their slow gradual elution (the analysis of K^+ ions does not allow for identification below the range of 30 mg/dm^3) from the sorbent (thus strong K^+ bonding), which prevents or at least limits the use of this system as a source of K^+.

The analysis of $PO_4{}^{3-}$ ion concentration shows that in the case of columns 1 and 2 (representing the mixtures: 1—R-SPA + raw HAL in the proportion of 1: 23 ± 5% and 2—V-SPA + raw HAL in the proportion of 1: 23 ± 5%), similar sorption effects were identified. The best effects of sorption of phosphate(V) ions were reported in column 3, representing the mixture: 3—R-SPA + V-SPA + raw HAL in the proportion of 1: 1: 23 ± 5%. In the case of column 1, the lack of phosphate(V) ions in reception 2 indicates the occurrence of a certain period of inhibition (lag-time) before the beginning of the elution of these ions from the system (or the initially very low effects of this elution). For reception 4, these ions are already analytically identified. In the case of column 2, the inability to identify the presence of phosphate(V) ions in test receptions 2 and 4 proves the possibility of extending this inhibition period, affecting the slow release.

In the case of column 3, on the other hand, the gradual elution of these ions is clearly identified, represented by the gradually decreasing concentration of phosphate(V) ions in test receptions 2 and 4, respectively. Thus, a technologically advantageous mechanism can be seen to ensure a smooth possibility of extending or shortening the inhibition period before starting the donation of phosphate(V) ions, regulated by the appropriate selection of the composition of the sorption mixture based on SPA and halloysite.

In the case of nitrate(V) ions, an increased concentration can be noticed in the excess solution. Nevertheless, it can be explained by independent sorption of pure water (swelling) and independent adsorption of ions dissolved (halloysite), which may lead to different final concentrations resulting from independent balances of water retained and nitrate(V) ions.

In each of the columns 1–3, a systematic decrease in the concentration of nitrate(V) ions can be observed, which proves their systematic elution and the presence of a relatively high concentration of these after receiving the 4th sample, corresponding to 4 weeks of simulated exploitation. The dynamics of elution of nitrate(V) ions from columns 1 and 3 are similar, while in the case of column 2, slightly higher (test reception 2) and slightly lower (test reception 4) concentrations can be observed.

The latest observation also proves the possibility of regulating the leaching rate of fertilizer components under dynamic conditions by using different compositions of polymer/halloysite, including R-SPA, V-SPA, and raw nanostructural halloysite species.

Observations for columns 4–6 indicate a weak desorption of magnesium Mg^{2+} ions. One can also notice the lack of or lower concentrations of potassium ions (below the range of the K^+ ion identification method <30 mg/dm^3) in the liquid samples corresponding to test receptions 2 and 4, respectively.

In the case of column 4, a systematic decrease in the concentration of phosphate(V) ions is observed in line with the desired technological concept. For column 5, the inhibition of the sustained release period corresponding to test reception 2 was observed (no possibility to identify these ions in the liquid sample), while in the case of column 6, the minimum concentrations of phosphate(V) ions were observed in the samples corresponding to test reception 2 and 4, which proves the low desorption abilities of this ion by column 6 (the lack of these ions in the sample of the separated excess after sorption, however, proves their favorable, nearly total (practical equilibrium) sorption).

For columns 4–6, a systematic, preferable slow release of nitrate(V) ions is observed. In the case of column 6, a larger concentration gradient of these ions can be seen for loads 2 and 4, which proves the possibility of their faster release and thus shortening the service life of the fertilizing function of the hybrid soil modifier. In the case of columns 4 and 5, the gradients of the decrease in the concentration of nitrate(V) ions during dynamic elution are already lower (possibility of longer operation), and in addition, higher concentrations in the case of the analysis of column 5 operation indicate the possibility of further longer operation of such a bed.

When analyzing the impact of different compositions of nutrient solutions on the mentioned need to find a technological compromise between the diversity of fertilizer ingredients in the solution and the physical sorption capabilities of this solution by the SPA, certain physicochemical relationships in the analyzed system described in the available literature should be taken into account [53].

Polymers like SPA have carboxyl groups in their chemical structure, which interact with certain parameters of the surrounding environment—an aqueous solution. These types of external parameters influencing the cyclic swelling/deswelling characteristic of SPA include, primarily, pH, the ionic strength of the surrounding solution, temperature, and the physicochemical properties of the solvent itself. In particular, the carboxyl groups present in the SPA structure are sensitive to the level and pH changes in the system. This causes SPA to behave like a non-ionic polymer at low pH values. But already, for higher pH values, it can be considered a polyelectrolyte [53].

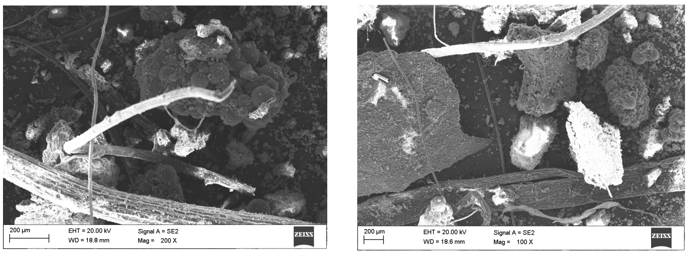
For low pH values, the polymer structure is shrunken, with increased mass packing density. This is because under these conditions, the polymer has a low charge density, as a result of which the chains are contracted or aggregated. Under these environmental conditions, the polymer–polymer interactions surpass the polymer–solvent interactions. However, when pH is increased, SPA shows a tendency to change towards polyelectrolyte (the carboxylic groups ionize) and swells, overlapping structurally and establishing a strong network with a gel-like characteristic. Some charges distributed along the polymer chain provide an increased solubility of the polymer (increased entropy of counterions). Simultaneously, the electrostatic repulsion between the charged groups contributes to the polymer volumetric expansion [53].

Polymer swelling phenomena are related to both electrostatic repulsion between the ionized carboxyl groups of the polymer and the osmotic pressure exerted by counterions. The potential presence of various hydrophobic groups in the polymer chain system may cause opposite tendencies responsible for reducing the swelling effects. For relatively high degrees of ionization, the effects of electrostatic repulsion are significant [53].

The swelling effect of SPA depends also on the presence in the surrounding solution of ions of different valencies. A particularly pronounced effect is observed in the case of divalent ions such as Mg^{2+}. This can be explained by the phenomenon of shielding electrostatic interactions by the electrolyte, which translates into the solubility of the polymer in the surrounding aqueous solution. For higher pH values, the polymer is partially deprotonated. The presence of divalent ions such as Mg^{2+} in the solution affects the shielding of the charges of carboxylic groups and, as a result, the deswelling of the polymer. Divalent ions are more effective for deswelling than monovalent ones [53].

3.4. SEM/EDS Analyses

Selected SEM images are presented in Figures 2–4.



(**a**) (**b**)

Figure 2. (**a**,**b**) Particle of R-SPA with surface-applied HAL particles in the 3D soil structure (SEM).

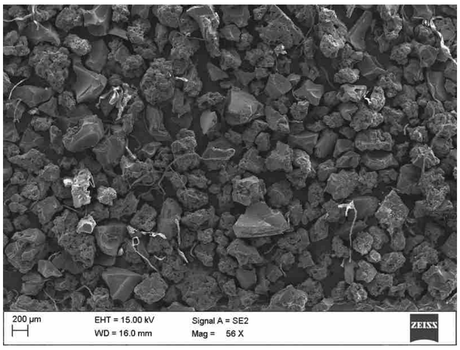


Figure 3. Primary unhydrated new halloysite grains mixed with SPA and cellulose fibers (SEM).

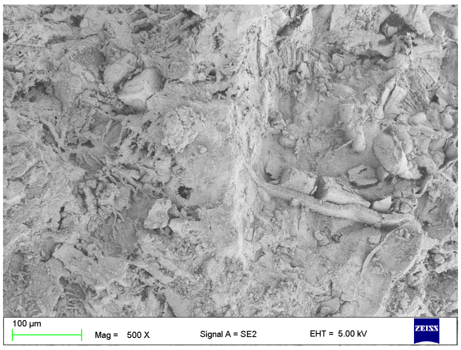


Figure 4. Structure of hybrid soil modifier after the tests—hydrated, dried, and hygienized R-SPA mixed with cellulose fibers from AHP and HAL (SEM).

Examples of SEM images of SPA particles with halloysite grains introduced on their surface are shown in Figure 5, whereas Figure 6 shows a SPA particle present in the soil environment.

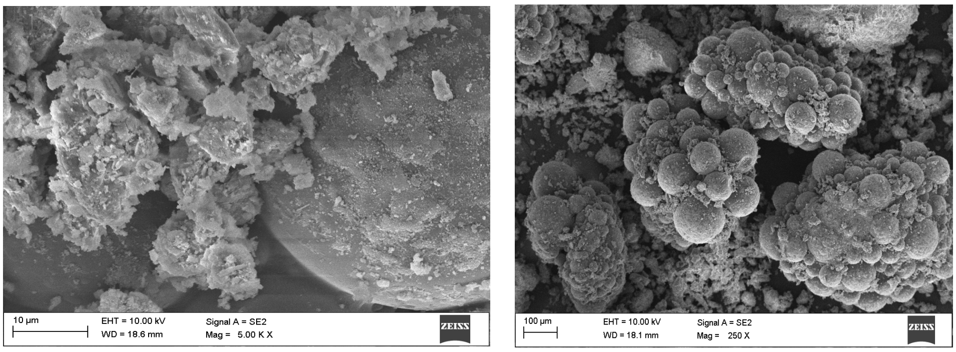


Figure 5. Structural details of the analyzed system containing SPA with halloysite grains—before the sorption of fertilizer substances in the tested system (SEM).

Figure 5 shows SEM images of the tested SPA particles (as characteristic regular spherical particles of larger size) with halloysite grains deposited on the surface (smaller particles distributed on the surface of larger spherical particles). In turn, Figure 6 shows SEM images of SPA particles introduced into the soil environment. A good fit of the SPA particles to the highly porous structure of the soil can be seen. This is potentially of great importance because the presence of SPA particles in the porous structure of the rhizosphere makes it possible to achieve some kind of stability in the plant-growing environment. Thus, a certain flexibility of the soil structure is achieved, as also noted in [11,12]. The presence of SPA in the structure of the rhizosphere also makes it possible to obtain more stable water retention conditions than only the use of the porous structure of the soil environment and horizontal/vertical transport of water in the soil based on capillary mechanisms. The introduction of SPA particles into the rhizosphere structure not only affects this structure but is also in a certain tension-force balance related to stress relaxation in this micro-environment. The SPA particles can absorb as much water as the free volume of the soil in which they are found allows, as well as to the extent that the relatively stiff structure of the rhizosphere allows the specific volume of the SPA particle to increase in volume. The interacting system of tension forces (dependent, among others, on the local physical structure and local mineral composition of the soil—of different local hardness) will be a decisive factor determining this retention mechanism, as well as the slow release of fertilizing substances. It is also related to the direct contact of the adsorbate on aluminosilicates with the locally released or penetrating water. Figure 6 shows exemplary results of the elemental EDS area analysis integrated with the SEM image of a SPA particle with halloysite on its spherical surface.

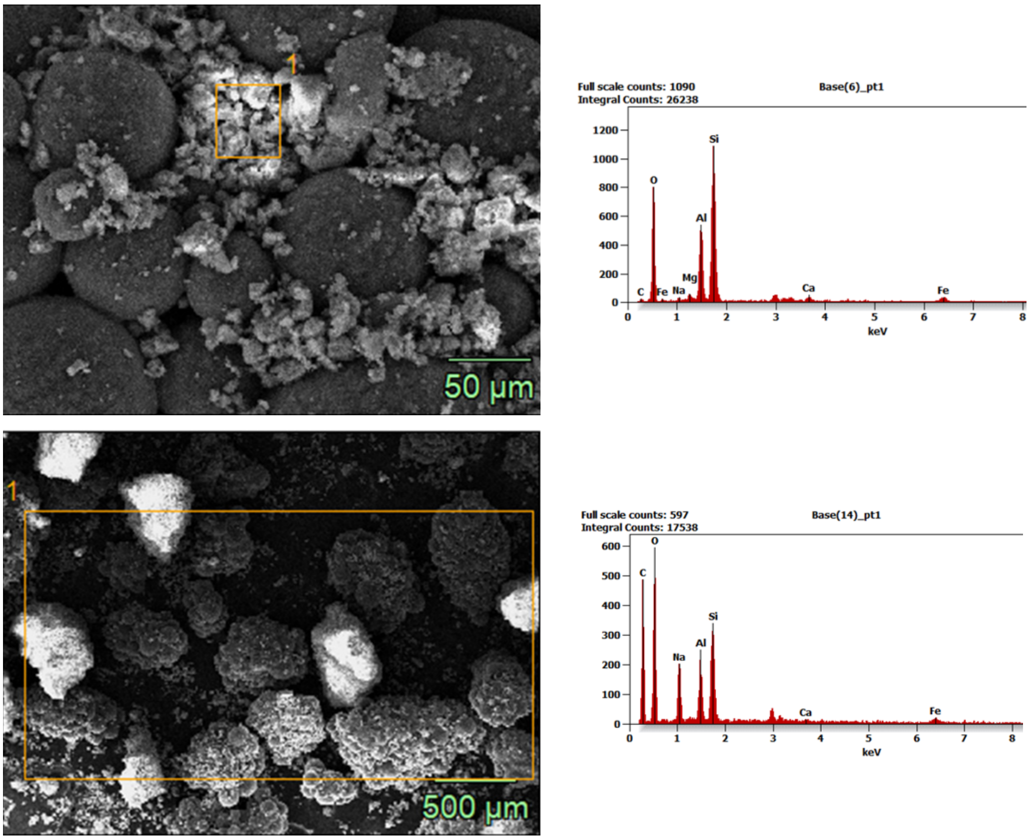


Figure 6. Exemplary results of SEM and elemental EDS area analysis regarding SPA particles with halloysite deposited on them in the soil environment (rhizosphere). 1—marked surface EDS analysis range used.

Based on the information in Figure 6, one can notice the presence of Al, Si, and O related to the chemical structure of halloysite. However, the presence of Na and C, as well as O, is related to the chemical structure of SPA ($(C_3H_3NaO_2)_n$). The presence of Mg, Fe, and Ca is related to natural admixtures in the halloysite geological deposit (Dunino, Poland).

The SEM/EDS analysis of SPA particles with surface-deposited halloysite adsorbent, directly in the tested soil environment, is shown in Figure 7.

In Figure 7, in addition to the elements related to the chemical structure of SPA particles (C, O, and Na) and halloysite particles deposited on its surface (Al, Si, and O), Fe, Mg, S, Cl, and Ca were also identified. Their presence may be related to other minerals naturally present in the natural halloysite geological deposit, substitutions of other elements in the halloysite structure, as well as the co-presence of other substances of both organic and inorganic origin in the complex natural soil structure (biomass fragments, other mineral fertilizers, etc.).

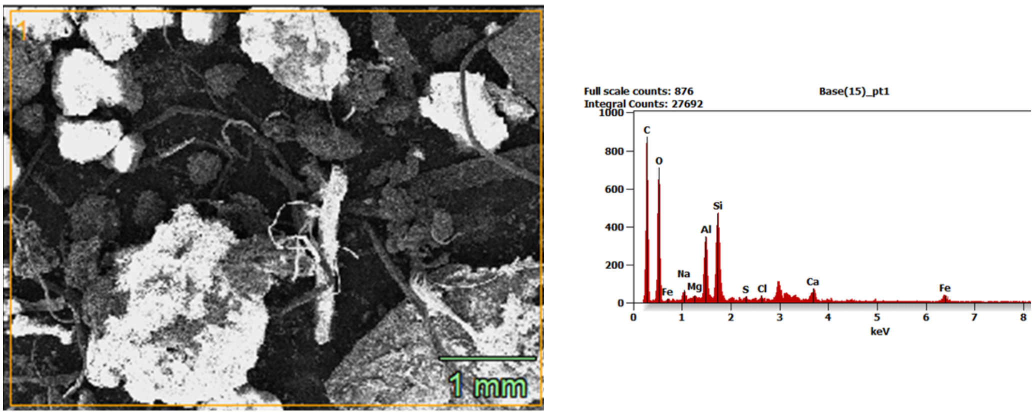


Figure 7. SEM/EDS analysis of SPA particles with surface-deposited halloysite adsorbent, directly in the tested soil environment. 1—marked surface EDS analysis range used.

4. Conclusions

In an approach to the issue consistent with CE principles, the authors proposed and verified the possibility of sustainable management of water resources and fertilizers using material resources available from a second processing cycle—as R-SPA. This approach provides an example of the possibility of practical application of the CE strategy in agriculture, which is a branch of industry necessary to meet the needs of each of the Earth's inhabitants.

The possibilities and technological restrictions of R-SPA derived from a selective recycling process for combined water retention and slow release of selected fertilizing substances were presented and critically evaluated based on our own experimental data. Due to the special physicochemical conditions related to the nature of the SPA polymer matrix and cross-linking processes significantly affecting the sorption capabilities, resulting directly from the chemical composition of the solutions (ion proportions affecting the ionic strength and pH), each solution must be experimentally verified.

The basic conclusions about technological importance can be formulated as follows:

1. The most beneficial effects of R-SPA swelling and water accumulation are achieved when it comes into contact with rainwater. This is a beneficial aspect, confirming the possibility of effective use of the original hybrid soil modifier in agricultural areas where the only source of water is natural atmospheric precipitation.
2. The clear impact of Mg^{2+} ions on the absorption capacity of R-SPA introduces the need for a technological compromise between the solution composition (N, P, K or N, P, K, Mg) affecting its fertilization value and the possibility of obtaining maximum R-SPA swelling, important for increased retention and slowed release of these ingredients.
3. The sorption capacity of R-SPA can be slightly increased by using R-SPA/V-SPA mixtures, but R-SPA still dominates in the system.
4. The possibility of technological adjustment of the leaching rate of fertilizer components under dynamic conditions by different combinations of (R-SPA/V-SPA)/HAL was demonstrated by column tests (dynamic leaching).

The presented research data have shown that selectively recycled R-SPA can be used as a part of a hybrid soil modifier, in particular for water retention in the rhizosphere layer. Due to the structural integration with Dunino halloysite responsible for the cyclic phenomena of adsorption and slow release of nutrients (desorption mode), repetitive sorption/desorption cycles in SPA located in the soil biosphere will generally be associated with the infiltration of rainwater (rain, snow), whereas its inseparable contact with the carrier of fertilizing substances (halloysite) makes the uptake of NPK(Mg) compounds possible.

The research purposefully focused on the integrated effect of the combined "retention, sorption and slow release", making it possible to estimate the net effect as an indicator directly determining the use of such systems in agriculture, forestry, horticulture, etc. The possibility of intentionally slowing the release of fertilizers into the rhizosphere is similar in concept to the struvite mineral fertilizer used in agriculture [54].

The use of R-SPA in the hybrid soil modifier also involves some additional technological limitations identified during the research. Due to the restrictive sanitary requirements, during preliminary sterilization of the R-SAP, optimal thermal conditions should be applied, both in terms of the effective elimination of harmful microorganisms and also in respect to preventing possible uncontrolled, spontaneous cross-linking processes that may adversely affect the future absorption capacity of the spongy R-SAP structure.

In the example of R-SAP and AHP's authors, the transformation process of a linear material cycle into a new, closed cycle. This approach provides an example of the possibility of practical application of the Circular Economy approach in agriculture.

The obtained results are the basis for a modern and innovative technology developed in accordance with the Circular Economy guidelines, combining both the market competitiveness of a hybrid soil modifier variant and contributing to the reduction of post-use SPA pollution in the natural environment on a global scale. It also helps solve the problem of diaper recycling, which accounts for several percent of the postconsumer waste stream by volume.

Author Contributions: Conceptualization, P.S., K.P. and M.R.; Methodology, P.S., K.P., S.C. and M.R.; Validation, P.S., K.P., M.R. and S.C.; Formal Analysis, P.S., K.P. and M.R.; Investigation, P.S., K.P. and M.R.; Resources, S.C.; Data Curation, P.S., K.P. and M.R.; Writing—Original Draft Preparation, P.S., K.P. and M.R.; Writing—Review and Editing, K.P., P.S. and M.R.; Supervision, S.C. and P.S.; Project Administration, S.C.; Funding Acquisition, S.C. All authors have read and agreed to the published version of the manuscript.

Funding: The research was conducted within the frame of Project No. RPSW.01.02.00-26-0032/18, entitled: "Construction of a pilot line and demonstration of the final form of an integrated technology for sequential processing of large-size and multi-material waste, in particular furniture and AHPs, as well as the production of an irrigation—fertilizing—sorption bed in P.P.H.U. TAMAX Tadeusz Cieślak" co-financed by the European Regional Development Fund under Task 1.2. "Research and development in the Świętokrzyskie entrepreneurship sector", Axis I "Innovation and science" of the Regional Operational Program of the Świętokrzyskie Voivodeship for 2014–2020.

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

Conflicts of Interest: Author Szczepan Cieślak was employed by the company "TAMAX" Ltd., Sędziszów, Poland. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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