

Article

From Fruit Waste to Hydrogels for Agricultural Applications

Akhmad Adi Sulianto¹, Ilham Putra Adiyaksa², Yusuf Wibisono³, Elena Khan⁴, Aleksei Ivanov⁴, Aleksandr Drannikov⁴, Kadir Ozaltin⁵ and Antonio Di Martino^{4,*}

¹ Environmental Engineering Study Program, Department of Biosystem Engineering, Faculty of Agricultural Technology, Universitas Brawijaya, Malang 65145, Indonesia; adi_sulianto@ub.ac.id

² Department of Biosystem Engineering, Faculty of Agricultural Technology, Universitas Brawijaya, Malang 65145, Indonesia; ilhamadiyaksa@gmail.com

³ Bioprocess Engineering Program, Faculty of Agricultural Technology, Universitas Brawijaya, Malang 65145, Indonesia; y_wibisono@ub.ac.id

⁴ Research School in Chemistry and Applied Biomedical Technology, Tomsk Polytechnic University, 634050 Tomsk, Russia; ivanovaa@tpu.ru (A.I.); aad12@tpu.ru (A.D.)

⁵ Centre of Polymer Systems, Tomas Bata University in Zlin, 760 01 Zlin, Czech Republic; ozaltin@utb.cz

* Correspondence: dimartino@tpu.ru

Abstract: Here, we describe and assess a method for reusing specific food waste to make hydrogels, which can be employed to improve the efficacy of agrochemicals and water. It represents an approach for tackling current challenges, such as food waste, water management, and pesticide optimization. Depending on the formulation, the hydrogels were created by crosslinking pectin and starch with CaCl₂ or sodium trimetaphosphate. FTIR and SEM were employed to investigate the methylation degree of the extracted pectin, as well as the surface morphology and interior structure of the hydrogels. The swelling behavior and water retention in sandy soil have been investigated. In addition to the hydrogels' potential to control and reduce pesticide loss, the herbicide Picloram is a model compound. The results show that the hydrogels have important swelling, up to 300%, and a capacity to retain water, preserve, and increase the water content in sandy soil up to 12 days. Picloram experiments show that hydrogels can limit herbicide mobility for up to 30 days under controlled conditions. The conversion of food wastes to highly valuable materials is a promising approach to optimize the water consumption and the loss of agrochemicals regarding sustainable agriculture.

Keywords: hydrogels; pectin; starch; food waste; soil management; Picloram



Citation: Adi Sulianto, A.; Adiyaksa, I.P.; Wibisono, Y.; Khan, E.; Ivanov, A.; Drannikov, A.; Ozaltin, K.; Di Martino, A. From Fruit Waste to Hydrogels for Agricultural Applications. *Clean Technol.* **2024**, *6*, 1–17. <https://doi.org/10.3390/cleantechnol6010001>

Academic Editor: Patricia Luis

Received: 27 November 2023

Revised: 21 December 2023

Accepted: 22 December 2023

Published: 27 December 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Agriculture is one of the most important industries and relies on water and nutrient supplies. Agrochemicals play an important role in agriculture as they (i) boost crop yield, (ii) fight plant diseases, (iii) enhance food quality, (iv) control pests and weeds, and (v) ensure stable production and high crop yield [1].

However, several drawbacks are related to their uncontrolled use, such as (i) soil and water pollution due to their mobility through the soil, (ii) soil degradation when beneficial microorganisms are killed, leading to poor-quality soil, and (iii) risks to human, animal, and insect health [2]. To reduce or better avoid soil and natural water pollution, a great deal of attention has been focused on developing new formulations of known compounds able to reduce leaking in soil and make them available for plants according to their needs. Among the various strategies and materials already in the market or under research, controlled release formulations based on hydrogels are receiving more and more attention. Hydrogels based on different polymeric materials have been tried as controlled-release vehicles for various agrochemicals. In controlled-release strategies, the agrochemicals are delivered over time at a specific rate from the treated surfaces, soil, or plants [3]. Advantages include longer application intervals, stabilization of the loaded compounds, and reduction

in dosages, toxicity, and risks regarding environment contamination as compared with conventional formulations, e.g., pesticides sprays [4,5].

Along with the use of agrochemicals, agriculture is heavily reliant on water, and a massive amount is required during irrigation. However, in some geographical areas or during dry seasons, water supplies and limited rainfall pose a severe problem that has a negative impact on crop stability. As previously stated, polymeric materials, especially hydrogels, are gaining interest due to their adsorbent capacity for regulating release and guarantee an adequate water supply during dry seasons.

Hydrogels can adsorb and hold a large volume of water due to their structure, which makes them a great material for storing water. The findings revealed that hydrogels offer a promising solution to today's agricultural needs. As reported, some of the main benefits coming from the use of hydrogels in agriculture are (i) reduction in the water volume for irrigation, (ii) reduction in leaking or mobility of fertilizers within the soil, with a consequent reduction in environment pollution, (iii) reduced plant death, (iv) enhanced plant growth, and (v) enhanced selectivity [6].

Currently, the majority of the hydrogels on the market are based on synthetic polymers because they have mechanical, physical, and chemical properties that may be tailored to meet particular requirements. However, there are some concerns about their biodegradability and the release of potentially harmful metabolites into the soil and groundwater [7]. For these reasons, hydrogels based on biopolymers such as polysaccharides have become more attractive.

Polysaccharides with superabsorbent capacity, such as starch [8], cellulose [9], chitosan [10], alginate [11], guar gum [12], gelatin [13], and pectin, have been employed as starting materials for the development of hydrogels for application in a number of fields, including biomedical, pharmaceutical, food and packaging, and agriculture, just to mention a few.

Due to the positive and promising results obtained from polysaccharides with hydrogels and polysaccharide-based hydrogels, attention has also been focused on the sources of polysaccharides, and one of the answers is coming from the food industry.

In the food chain, a huge volume of waste is produced during all the phases from growing to harvesting to the table. Peels are one of the major byproducts coming from the processing of different fruits. Generally, as they are not used, they represent a solid waste, which is mostly dumped. Despite that, they are rich in important chemical components, and some of them have high value due to their intrinsic properties, such as polysaccharides. Finding a way in which to use and valorize such resources instead of dumping them has both an economic and environmental impact [14].

Pectin is a key polysaccharide found in orange and apple peels, and its level can reach up to 35% in some types of oranges, making them a useful source for pectin extraction [15].

Pectin is a polysaccharide that comes from higher plants' main cell wall and intracellular layer [16]. It consists of an α -(1,4)-linked polygalacturonic acid backbone that is interrupted by rhamnose residues and neutral sugar side chains. The carboxyl groups of pectin's galacturonic acid residues are susceptible to being esterified with methyl or acetyl groups, and pectin is classified as low- or high-methoxyl (LMP DM 50%; HMP DM > 50%) according to the degree of methyl-esterification (DM). Pectin hydrogels have a wide range of uses because of their special structure, flexibility, high water content, and biocompatibility [17]. Furthermore, compared to gels made from other gel-forming biopolymers like gelatin, pectin gels perform better in terms of gelation duration, melting point, carrier, and fat barrier qualities [18].

Like orange and apple, banana peels represent a waste source. In some types of bananas, starch can represent up to 30% of the dry peel mass, making them a valuable starch source.

Starch is a storage polysaccharide in plants and consists of a number of monosaccharides combined with a -D-(1-4) and or a -D-(1-6) linkages [19]. Depending on the source (corn, potato, tapioca, or wheat), the proportions of the two main structural compo-

nents of starch—amylose and amylopectin—vary [20]. Meanwhile, amylopectin is heavily branching, and amylose is linear or only slightly branched. Starch can be chemically modified for nonfood applications to produce materials with desirable qualities for a range of uses. The starch molecules may be modified by adding hydrophobic or ionic groups, which would alter their viscosity and association behaviors [21]. Starches are suitable for making composite hydrogels because of their high hydroxyl group content. Both starch and starch-based hydrogels have benefits and drawbacks. The benefits include being a plentiful and renewable resource that can be found in various locations, being attractive and economically viable, having a high swelling capacity in water, being an amphiphilic crosslinked adsorbent, as well as being able to be used in a range of processes. On the other hand, disadvantages include poor surface area and the necessity for chemical derivatization to improve sorption capabilities [22]. It appears that the benefits of adopting starch, particularly its biodegradability, outweigh the risks. This is due to the recent focus on reducing environmental issues created by the use of synthetic polymers.

The primary goal of this scientific work is to propose and suggest a strategy for valorizing selected organic food waste, such as oranges, apples, and banana peels, for the development of hydrogels with the objective of boosting the efficacy of water and agrochemicals while minimizing their environmental impact. We did not focus on the extensive chemical characterization of the pectin and starch extracted. At this phase of the research, our preliminary scope is to evaluate the feasibility of the approach and the performances of the produced materials extracted from food waste. The materials' detailed characterization and the association between the chemical structure of extracted pectin and starch, their interaction, and the hydrogel properties are currently being investigated.

2. Materials and Methods

2.1. Materials

Pectin was extracted from orange (tangerine) and apple (red delicious) peels, while starch from banana (cavendish). Citric acid, sodium metabisulphite, calcium chloride, sodium hydroxide and the Picloram herbicide (PESTANAL[®] Sigma Aldrich, Taufkirchen, Germany), Polyvinyl Alcohol hydrolyzed (PVA Mw 30.000), sodium trimetaphosphate, and sodium metabisulphite were purchased from Sigma Aldrich (Germany). All chemicals used were of reagent grade and were used as received without any further purification.

2.2. Extraction of Pectin from Apples and Oranges Peel

Pectin was extracted from orange and apple peels as schematically indicated in Figure 1. In brief, 800 g of orange and 800 g of apple peels were washed with tap water and then dried in oven at 70 °C until a constant weight was reached. The obtained dried biomass was displaced in a 10 L beaker containing a citric acid aqueous solution (pH 1.5) at solid:liquid ratio of 1:10. The solution was heated at 80 °C and mechanically stirred for 40 min and then filtered to remove the solid part [23]. Afterwards, ethanol was added to the filtrated solution and pectin let precipitate for 12 h. The solution was again filtered by a filter cloth, the pectin recovered and dried in oven at 60 °C for 36 h, and then reduced in powder mechanically.



Figure 1. Schematic representation of the pectin and starch extraction from orange, apple, and banana peels.

2.3. Extraction of Starch from Banana Peel

Starch was extracted from banana peels following a reported procedure [24]. Firstly, 1600 g of banana peels were weighed, washed with tap water, cut in small pieces (Figure 1), and dried in oven at 70 °C until a constant weight was reached. Afterwards, a solution of 0.2% sodium metabisulphite was added at *w/v* ratio 1:2 to the dried biomass. The solution was homogenized using a goldleaf X1740 homogenizer for 25 min and then filtered by a cotton filter. The sediment, which is the starch, was recovered and dried in oven at 60 °C for one day and then reduced to powder using a laboratory mill.

The extraction yield of pectin and starch was calculated by dividing the weight of the dry extract by the weight of the dry biomass, orange + apple peel and banana peel, and multiplying by 100, respectively.

2.4. Preparation of Pectin-and-Starch-Based Hydrogels

Three set of hydrogels were prepared and labelled as follows: PEC (pectin hydrogel); STA (starch hydrogel); and PEC–STA (pectin–starch 1:1 *w/w* hydrogel).

Pectin hydrogels were prepared using CaCl₂ as crosslinking agent [25]. At first, pectin powder was dissolved in distilled water (5% *w*) by mechanical stirring at room temperature. Once totally dissolved, an aqueous solution containing 10% of CaCl₂ was added, the mixture stirred for 10 min, and then stored for 24 h at room temperature. After that, an aqueous solution of NaOH (10% *w/v*) was added to the mixture followed by 10 mL of methanol to allow the precipitation. After 12 h, the solution was filtered, the gel recovered, and frozen at –20 °C before being dried under vacuum.

2.4.1. Starch Preparation by Thermal Approach

The starch hydrogels were prepared by heat gelatinization, following a reported protocol with minor modifications [26]. Moreover, 2 g of dry starch powder were poured in 15 mL of distilled water and heated at 90 °C for 25 min and then cooled to 50 °C. Then, a 10% *w/v* solution of PVA (Polyvinyl alcohol) was added and kept to 55 °C for additional 30 min. The obtained paste-like product was frozen at –20 °C and dried under vacuum.

2.4.2. Pectin–Starch Hydrogels

The composite pectin–starch hydrogel, at weight ratio 1:1, was prepared following a reported procedure [27]. Two solutions were prepared, one containing 25 g of pectin and the other with 25 g of starch, both in 500 mL of distilled water. The two solutions were mixed and left under vigorous mechanical stirring for 30 min and then the crosslinking agent sodium trimetaphosphate was added. The solution was stirred for additional 15 min and then stored at room temperature for 12 h. Afterwards, the hydrogel was removed, frozen, and then dried under vacuum.

2.5. Mechanical Properties of the Hydrogels

The mechanical properties of hydrogels were determined by a Texture analyzer (TA.XTplusC Stable Micro Systems, Surrey, UK) following a reported protocol [28]. Fully hydrated hydrogels were cut into a cylindrical shape with a diameter of 10 mm and a thickness of 2 mm. The compressive tests were carried out using a 1 kg F load cell and at strain rate of 0.05 mm/s. For each experimental condition, 5 specimens were tested. The compressive modulus was calculated from the slope of the initial linear portion of the stress–strain curves, while the toughness from the area under the curve. Young's modulus (*E*) was calculated by the equation [28]

$$E = \frac{F/A}{\Delta H/H} \quad (1)$$

where the ratio F/A is the applied force (N) per surface unit and $\Delta H/H$ is the uniaxial deformation. The compressive strength was obtained by

$$Q_t = F/A \quad (2)$$

where F is the force (N) measured during compression and A is the cross-sectional area (mm^2) of the probe [28]

The mechanical properties were measured in “fresh” hydrogel (immediately after preparation and labelled as day 0) and after 21 days grounded in the soil (labelled as day 21) to estimate their variation during the permanence in the soil.

2.6. Surface Morphology and Inner Structure of the Hydrogels

The variation in the surface morphology and the internal structure of the hydrogel before and after being buried for 21 days in soil at 75% RH and 27 °C were studied by scanning electron microscope (Nova NanoSEM 450 (FEI), Sydney, Australia). Prior to the analysis, the wet hydrogels were frozen at -20 °C for 24 h and then lyophilized for 24 h, while the buried hydrogels were cleaned to remove soil residues and left in oven at 70 °C for 12 h to remove possible moisture. The hydrogel samples were then sputtered with a layer of gold.

2.7. FTIR Analysis

The FTIR spectra were recorded on IR Affinity-1S spectrophotometer (Shimadzu, Japan) equipped with a single reflectance ATR diamond. The spectra were collected at 32 scans with resolution at 1 cm^{-1} . All the spectra were recorded in the range $4000\text{--}400 \text{ cm}^{-1}$ using a straight baseline.

The methyl esterification (DM) content in pectin was calculated following a described method [29]. The linear correlation coefficient for the calibration curve was $R^2 = 0.9593$.

2.8. Methylation Degree of Extracted Pectin

The methylation degree (DM) of pectin samples was evaluated using a titration method according to a previously published protocol [29]. The dried pectin was weighed (0.1 g) and wetted with 95% ethanol. Following that, 10 mL of distilled water was added at 40 °C and stirred at 200 rpm for 2 h to allow the pectin to dissolve. Then, the solution was titrated with 0.1 N NaOH. As an indicator, phenolphthalein was utilized. After that, an additional 5 mL of 0.1 N NaOH solution was added, and the solution was agitated for an additional 2 h for saponification of the polymer’s esterified carboxylic acid groups, and 5 mL of 0.1 N HCl was then added.

The following equation was used for calculating the DM [29]:

$$DM(\%) = \frac{V_0}{V_0 + V_f} \times 100 \quad (3)$$

where V_0 refers to the volume (mL) of 0.1 N NaOH solution for the first titration and V_f is the volume (mL) for the second titration.

2.9. Measurement of Water Absorbency

The water absorbency was measured by the filtration method at room temperature (23 ± 1 °C) [30].

A series of tea bags filled with 100 mg of dried hydrogel samples were immersed in tap water at room temperature. The samples were let to swell until the equilibrium was reached, then separated from the media and the surface fluid removed by adsorbent paper. The water absorbency, Q , of sample was calculated according to following equation:

$$Q(\%) = \frac{A_s - A_d}{A_d} \times 100 \quad (4)$$

where A_d and A_s are the weight (g) of dry and swollen sample, respectively. Q was calculated as grams of water per gram of dry hydrogel [30].

2.10. Soil Moisture Content

The possibility to use hydrogel based on the extracted polysaccharides to reduce the negative effects of drought stress was tested using sandy loamy soil. Each hydrogel formulation (2 g/kg of soil) was added to 10 kg soil in a plastic pot. All the pots were irrigated at 100%, 75%, 50%, and 25% of the maximum capacity. The soil water content expressed in percentage (SWC) was calculated using the following formula:

$$SWC (\%) = \frac{S_W - S_D}{S_D} \times 100 \quad (5)$$

where (S_W) is the weight (g) of the wet soil and (S_D) the weight of the soil after dried at 85 °C for 4 days.

2.11. Determination of Water Retention Efficiency

The determination of water retention efficiency was evaluated as follows: a plastic pot was filled with 2 kg of sandy soil (properties are in Table 1), and 4 g of each hydrogel formulation (starch, pectin, and pectin + starch) was mixed with the soil and the weight of the pot recorded (R_i). All the pots reached saturation in three hours; 1 h following the saturation, the weight of pot was recorded and listed as time zero at zero time (R_0). All the pots were weighted at determined time intervals 2, 4, 6, 8, 10, 12, and 14 days (R_t). Then, using the following formula, the water retention expressed in percentage was calculated.

$$R(\%) = \frac{R_0 - R_t}{R_0 - R_i} \times 100 \quad (6)$$

where R (%) is the water retained in percentage, R_t the weight (g) at time t , R_i the initial weight (g), and R_0 represents the weight (g) at time zero.

Table 1. Properties of the sandy soil used in all the experiments. PWP (permanent wilting point); CEC (cation exchange capacity); OM (organic matter).

Soil Properties	Value
Sand (%)	95
Silt (%)	6
Clay (%)	4
Bulk Density (mg/m ³)	1.55
PWP (%)	7.35
Conductivity (ds/m)	2.4
pH	7.8
CEC (cmol/kg)	4.27
OM (%)	0.09
CaCO ₃ (%)	4.16

2.12. Porosity

The hydrogel's porosity was roughly estimated by the solvent replacement method. Ethanol is a nonsolvent for pectin and starch when the hydrogels are soaked in it; it tends to fill the pores and the free spaces within the hydrogel structure. Sphere-shaped hydrogels were prepared, dried, and then the weight recorded. After that, the hydrogel was immersed for 24 h in nondenatured ethanol, then removed, wrapped in tissue paper, and then the weight recorded again. The porosity (P), expressed in percentage, was obtained as follows:

$$P(\%) = W_{24} - W_0 \rho V \times 100 \quad (7)$$

where W_0 and W_{24} are the weights (g) of the hydrogel before and after immersing in ethanol, respectively, while ρ is the density (g/cm^3) of ethanol and V the bulk volume (cm^3) of the hydrogel [31].

2.13. Retention Rate of Picloram in Soil

The retention rate of the herbicide Picloram in sandy soil was investigated for each hydrogel preparation. In brief, four plastic pots were filled with 1.5 kg of sandy soil. One was the control, while the others were mixed with 5 g of dried PEC, 5 g of STA, and in the last 5 g of PEC–STA hydrogel separately. The hydrogel had the shape of spherical granules. To each pot, 1500 ppm of Picloram was added and then 500 mL of tap water poured. The Picloram concentration was monitored every 3 days for a total period of 30 days. The herbicide extraction from the soil was performed following a reported protocol with minor modification [32].

In brief, 100 g of soil was mixed with 100 mL of 2 N KCl solution, shaken for 1 h, and then centrifuged at 2000 rpm for 10 min. The supernatant was recovered, decanted, and then analyzed by HPLC (Shimadzu Prominence LC 20AP/FRC-10A, Kyoto, Japan). The HPLC conditions used were the following: as mobile phase a water solution acetic acid (2%)/acetonitrile (95/5 *v/v*), 500 μL injection volume, and flow rate of 1000 $\mu\text{L}/\text{min}$. The wavelength used to detect Picloram was 254 nm.

2.14. Biodegradation in Soil

The experiments were conducted in plastic pots (8 cm diameter and 15 cm height), which were filled with sandy soil up to 80% of the total volume capacity. The hydrogel samples were cut in square shape, dried in oven at 70 °C, weighted, and buried at 5 cm deep to maintain aerobic conditions for degradation. The pots were placed in a controlled chamber at RH 75% and temperature 27 °C. The hydrogel weight was checked at determined time intervals and the biodegradability, expressed in percentage, calculated by using the equation

$$\text{Biodegradability (\%)} = \frac{M_0 - M_t}{M_0} \times 100 \quad (8)$$

where M_t and M_0 are the weights (g) of the samples at certain time and initial time, respectively.

3. Results

3.1. Extraction Yield

The extraction of starch and pectin is determined by mass transfer into the process medium, and the yield and quality of the extracted products define the effectiveness of the technique [33]. Many factors affect pectin and starch extraction yield, including the starting biomass, technological processes, including grinding and size of particles, the temperature, solid:liquid ratio, equipment, and operational procedures. In this research, we extracted pectin from tangerine oranges and red delicious apple peels and starch from Cavendish banana peels.

The weight of the wet and dry biomass, the amount of water it has, and the yield of pectin and starch are summarized in Table 2.

Table 2. Biomass type, weight, and polysaccharides' yield.

Biomass	Wet Weight (g)	Moisture Content in the Biomass (%)	Dry Weight (g)	Polysaccharide Yield (g)/(%)
Orange peel	800 ± 10	82 ± 1	144 ± 1	Pectin
Apple peel	800 ± 10	76 ± 2	192 ± 1	87/26%
Banana peel	1600 ± 10	85 ± 1	240 ± 1	Starch 31/13%

The pectin obtained from orange and apple peels was not separated in this study as the extraction was carried out by mixing the orange and apple peels. The choice was made because it was not needed at this point of the process to understand from where more pectin was obtained and the differences in chemical structure. However, as was previously noted [34], it is assumed that the majority of the pectin content is derived from the orange peels, which can account for up to 30% of the dry weight. In the case of the apple, it is limited to 2% [35]. It has to be added that the content of pectin varies with the type of apple or orange considered, while the yield is strictly connected with the extraction procedure. The same is true for the starch content in banana peels.

3.2. Hydrogels' Characterization

Three sets of hydrogels, based on two components, pectin and starch, were prepared and their physical–chemical and mechanical properties evaluated.

3.2.1. FTIR Spectra

In the FTIR spectrum (Figure 2) of the pectin hydrogel (PEC), the peak at 3300 cm^{-1} is ascribed to O-H stretching pertaining to the following: at 2900 cm^{-1} , range $1600\text{--}1800$, and $1100\text{--}1300\text{ cm}^{-1}$ for C-H stretch, C=O stretch, C-O stretch for esters or carboxylic acid, and C-N stretch [36,37]. The spectrum of banana starch hydrogel (STA) has a characteristic peak at around 900 cm^{-1} related to characteristic starch structure. The peaks at 1390 , 1660 , and 2350 cm^{-1} are ascribed to O-H bending, C-C aromatic ring stretching, and C-H stretching, respectively [38]. In the spectrum of the composite hydrogel based on the equal content of pectin and starch (PEC–STA), the main peaks of pectin and starch are observable.

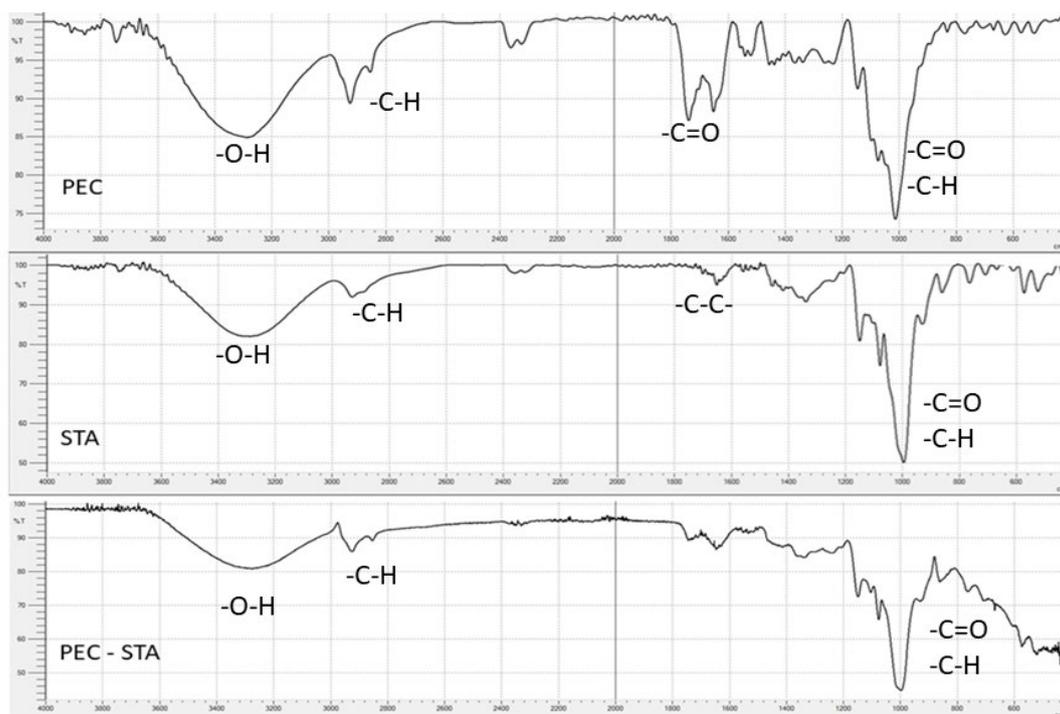


Figure 2. FTIR spectra of hydrogels based on pectin (PEC), starch (STA), and composite pectin–starch (PEC–STA). The Y- and X-axes refer to the transmittance (%T) in percentage (%T) and the wavenumber ($4000\text{--}400\text{ cm}^{-1}$), respectively.

The methylation degree of the extracted pectin was calculated following a reported method and resulted to be 65%, meaning that the pectin is considered as high-methoxy [36].

3.2.2. Mechanical Properties

Many factors influence the mechanical properties of hydrogels, including the chemical structure, molecular weight, crystallization of the polymer, network topology, crosslinking nature, and density. In this study, we simply tested and compared the toughness, compressive strength, and Young's modulus of various hydrogel formulations.

The composite hydrogel (PEC–STA) demonstrates a significantly greater compressive strength than the monocomponent PEC and STA. Toughness and Young's modulus additionally exhibit an increase but of lower magnitude. Despite the fact that polysaccharide hydrogels are known to have weak mechanical properties when compared to synthetic polymeric materials, the improvement in PEC–STA properties is probably attributed to the combination of crosslinking and interactions, especially the hydrogel bonds between the hydroxyl groups displaced along the pectin and starch backbones. Indeed, in addition to intra- and intermolecular interactions between PEC and STA, there are PEC–STA interactions in the composite hydrogels that help to maintain the structure. Furthermore, we expect that, in addition to the crosslinking points formed by the crosslinking agent, chain entanglements between polysaccharide chains also indicate additional crosslinking points. The number of crosslinking points directly influence the hydrogels' properties in terms of swelling, ability to release water, etc. Figure 3B shows a significant decline in the values measured in the hydrogels after being buried in soil for 21 days. It can be explained by the influence of biodegradation, which results in the production of pores of various dimensions, which alter the mechanical properties (Figure 3A,B). As can be seen, the area of the hydrogel is reduced in all the formulations, but those based on starch show a more significant reduction, which is probably due to starch's quicker biodegradation kinetics.

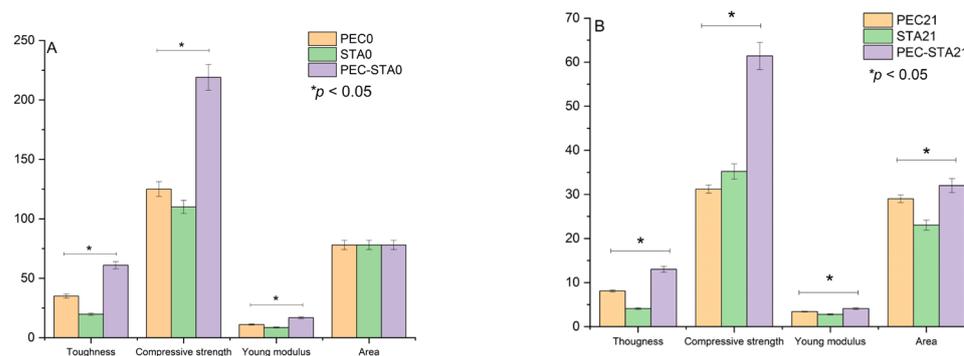


Figure 3. Mechanical properties of the hydrogels' formulations at (A) day 0 and (B) after 21 days buried in soil ($n = 3$). In the Y-axis, the numerical values of toughness (kJ/m³), compressive strength (kPa), Young's modulus (kPa), and area (mm²) are reported. The data refer to the average value \pm SD. All the experiments were performed in triplicate.

3.2.3. Hydrogel Porosity

Pores can form in hydrogels either by separating phases during preparation or as smaller pores in the network. According to the pore size, the hydrogel materials are classified in four main categories: (i) superporous (pore size > 100 μ m), (ii) macroporous (pore size 0.1–1 μ m), (iii) microporous (pore size 0.1–0.01 μ m), and (iv) nanoporous (pore size 0.001–0.01 μ m) [39]. The porosity, together with the pore size, play an important role in the biodegradation in soil.

Herein, we did not evaluate the size of the pores and the distribution but only estimate the porosity in percentage using the solvent displacement approach. The porosity of all the hydrogel formulations in the fresh state (defined as day 0) and after 21 days buried in the soil was estimated to also understand the possible mechanism involved in the biodegradation, supported by the microscope investigation and mechanical properties evaluation (see Figures 3–5).

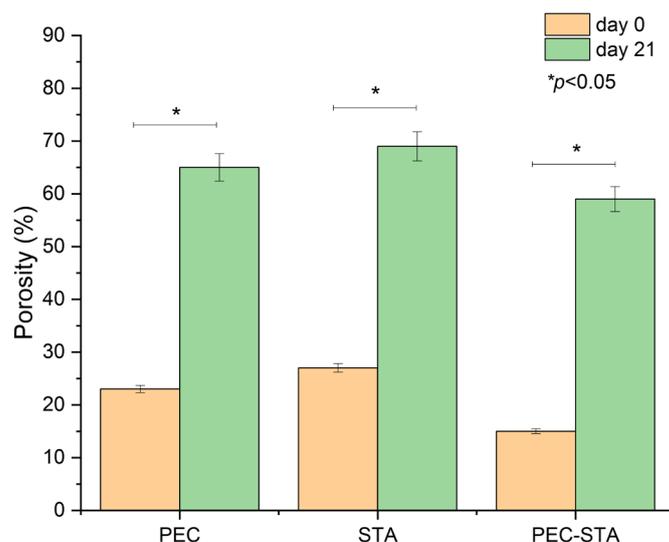


Figure 4. Porosity of the three hydrogel formulations at day 0 and after 21 days buried in soil ($n = 5$). The data refer to the average value \pm SD. All the experiments were performed in triplicate.

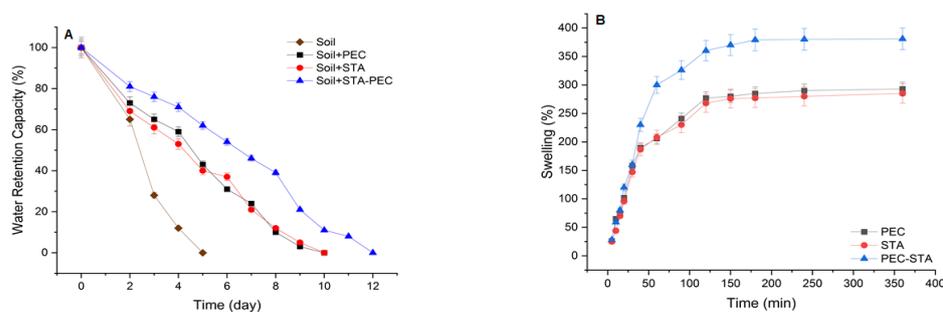


Figure 5. (A) Water retention capacity of soil with and without hydrogels; (B) swelling capacity. The data refer to the average value \pm SD ($n = 3$).

The porosity of the formulation of the three hydrogels is estimated from the data in Figure 4. At day 0, the porosity is highest in the PEC and STA compared to the composite PEC–STA. Different intermolecular interactions in addition to a higher crosslinking density could be the cause. While in PEC and STA formulations there are only homogeneous intra- and intermolecular interactions, in the PEC–STA composite, there are also heterogeneous interactions and additional chain entanglements between PEC and STA, which could contribute to enhancing the crosslinking density. After 21 days in soil, the porosity drastically increases in all the formulations. This can be attributed to the biodegradation, suggesting that the mechanism involves formation of pores and consequently loss of weight and mechanical properties, as supported by the data in Figure 6. Considering that a traditional approach has been used for the extraction, the obtained yield can be considered positive. An increase in the yield can be reached using nontraditional approaches or by using US and/or microwaves.

3.2.4. Swelling and Soil Water Retention

Swelling is the process of penetration of solvent molecules into a polymer matrix, causing an increase in the volume, while negative swelling (shrinkage and hydrocollapse) is the opposite phenomenon, where a reduction in the volume is observed after absorption of a solvent. Positive and negative swelling, however—the ability to adsorb a large volume of water and then release it over time at a certain rate—make hydrogels useful tools in agriculture.

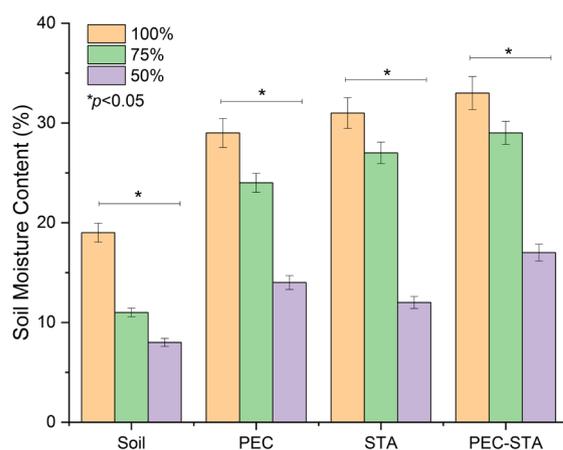


Figure 6. Effect of the hydrogel on the soil moisture content. The data refer to the average value \pm SD. All the experiments were performed in triplicate.

Sandy soils are characterized by low water retention capacity and excessive drainage of rain and irrigation water below the root zone, resulting in inefficient water and agrochemicals use [40]. Therefore, increasing the total amount of water that a soil can hold and available water capacity (the amount of water that a plant can uptake) is vital to ensure efficient water use and sustainability [41]. The development of nontraditional practices to improve the retention and water capacity of light soils is gaining more attention, in particular by using superabsorbent materials.

Figure 5A demonstrates the ability of the hydrogels to retain water in soil. The water retention at 5 days of irrigation is assessed between 40 and 45% for the pectin and starch hydrogels, while it is 62% in the case of the pectin–starch hydrogel. Simultaneously, the control (soil) shows almost 0% water retention, indicating that all the water poured has been leaked. The data clearly demonstrate the benefits of hydrogels in improving the water retention of sandy soil. The best performance of the pectin–starch hydrogel in enhancing water retention is related to swelling behavior. Pectin and starch hydrogel demonstrate a water retention higher than 20% up to one week and PEC–STA hydrogels up to 9 days.

The trends in Figure 5B show the swelling behavior of the hydrogels in relation to their polysaccharide composition. In all the formulations, two main phases can be observed: an initial fast swelling followed by a gradual decrease until reaching the equilibrium point, maximum swelling. In the initial phase, the swelling reaches up to 190% for pectin, 187% for starch, and 230% in the hydrogel created by a pectin–starch combination. In addition, after 50 min, in the pectin and starch hydrogel, the swelling rate is reduced until equilibrium in the mixed hydrogel, continuing to rise up to 300%. All the formulations reach the equilibrium within 150 min from contact with the media. The maximum swelling was found to be 293% for pectin, 285% for starch, and 381% for pectin–starch.

In accordance with previously published results, the values in Figure 6 can be attributed to the polymeric material's capacity to adsorb and gradually release water by diffusion once the level of moisture in the surroundings is reduced [42].

Figure 6 shows the moisture content of sandy soil measured at regular time intervals. The results show that, when hydrogels are applied, the soil moisture content increases compared to the control, pure soil. The data, along with those presented in Figure 5A,B, confirm the beneficial impact of hydrogels in retaining water and improving the moisture content in sandy soil. The swelling and water retention capacities of composite hydrogels based on the combination of PEC and STA exhibit a significant increase. The inner structure generated by the spatial displacement of the chains, as well as their intra- and intermolecular interactions, lead to greater capacity to allocate and preserve water molecules. It should be noted that, due to the nature of the substances employed, particularly pectin, swelling is pH-dependent and can differ with the pH of the water, whereas those linked to water

retention in soil may vary depending on the nature of soil, temperature, and humidity. Comparable results were observed in previous investigations, in which polysaccharides were used to enhance water retention and soil humidity [43,44].

3.3. Biodegradation in Soil

In recent years, there has been increased interest in the use of hydrogel materials to enhance soil water management. Their performance as soil amendments depends on the stability in soil. In fact, biopolymer-based hydrogels, like polysaccharides, are considered environmentally friendly due to their apparent fast biodegradation without release of toxic components in the soil, as opposed to their synthetic counterparts. However, the fast biodegradation can have a certain impact, sometimes negative, when long-term performances in adsorbing and releasing water or other components, e.g., agrochemicals, are considered. There are several ways to measure the biodegradability of hydrogels in soil. The soil burial method is a common way to investigate the biodegradability of a hydrogel in soil [45,46].

Biodegradation in soil is influenced by soil factors such as moisture content, aeration, and the presence of organic matter, as well as the nature and chemical and physical properties of the hydrogels [47,48]. Because of the appropriate conditions, biodegradation from microbial activity begins earlier in wet dirt than in dry dirt. The patterns in Figure 7A,B demonstrate the percentage biodegradation and weight loss over time of the hydrogel buried in sandy soil at 75% RH and 27 °C. The trends indicate that STA biodegrades faster, implying that they are less stable in the examined conditions. Because starch is a hydrophilic polymer, it swells continuously over time. The presence of easily accessible water organic carbon sources promotes microbial activity, which accelerates biodegradation, leading to the collapse of the hydrogel's network [49]. Combining starch with other polymers while maintaining its content minimal is one strategy to reduce the high breakdown rate [50].

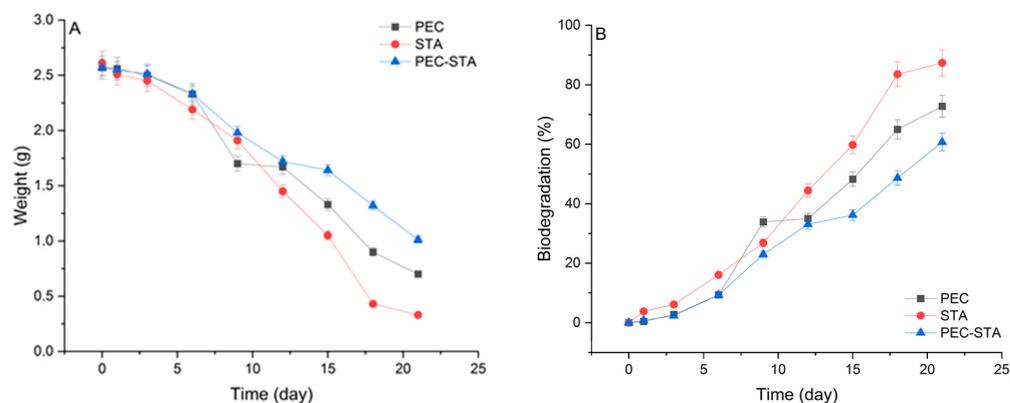


Figure 7. Biodegradation studies expressed as (A) variation in hydrogels' weight over time buried in moist soil and (B) biodegradation of the hydrogel over time ($n = 5$).

Compared to starch, the chemical structure of pectin is more complicated as it contains different monosaccharides linked together by different linkages. The structure of pectin is generally reported as so-called "smooth" and "hairy" regions. The smooth regions contain linear chains of homo- or heteropolymers, whereas the hairy regions contain simple or complex side chains. Due to the complexity of the pectin structure, the degradation of pectin in nature occurs by de-esterification, followed by hydrolytic cleavage of the α -1,4-glycosidic linkages that exist in the backbone of the pectin substrate.

The mechanism of microbial degradation of pectin differs with the type of enzyme involved in the process [51]. The following are some mechanisms of action of enzymes involved in pectin degradation:

- (a) Mechanism of de-esterification by pectin esterase and pectin methyl esterase—for example, a multi-attack mechanism—which is then followed by the decomposition of the oligomers to release the products;
- (b) Mechanism of hydrolytic cleavage in polygalacturonases and pectin lyases.

Herein, biodegradation has been estimated as the change in weight during that time as it represents a very common and simple approach. Together with loss in weight, the variations in surface morphology and inner structure were also evaluated by SEM microscope at day 0 and after 21 days buried in the soil (Figure 7A,B).

The trend in Figure 8A shows how dried STA loses weight faster than PEC, with a drop of over 80% after 21 days against 68% for PEC. PEC–STA composite hydrogel exhibits greater stability in soil and under the explored conditions, with a weight reduction up to 50%. Considering the potential enzymatic biodegradation mechanism, we hypothesize that the PEC–STA blend creates a structure that is less accessible to microbial enzymes, which are mostly responsible for bond breaking, and consequently limits the biodegradation rate. The scanning electron microscopy (SEM) pictures in Figure 8 suggest that biodegradation starts in the bulk, with the formation of holes that tend to expand in size over time. It means that degradation happens in phases, starting with a change in the inner structure. As expected, an increase in porosity causes a considerable decrease in the mechanical properties of the hydrogels (Figure 3). Such a mechanism has also been observed in previous studies dealing with polysaccharide-based hydrogels in which pores emerge after being buried in wet soil for weeks [52]. Combining weight change with pore formation, it is clear that STA hydrogels, which seem to have greater porosity, also have higher weight loss compared to the composite pectin–starch. It could be connected to increased enzymatic hydrolysis [53], confirming the notion that the interior structure and the development of additional crosslinking points could decrease enzyme access to active sites throughout the chains.

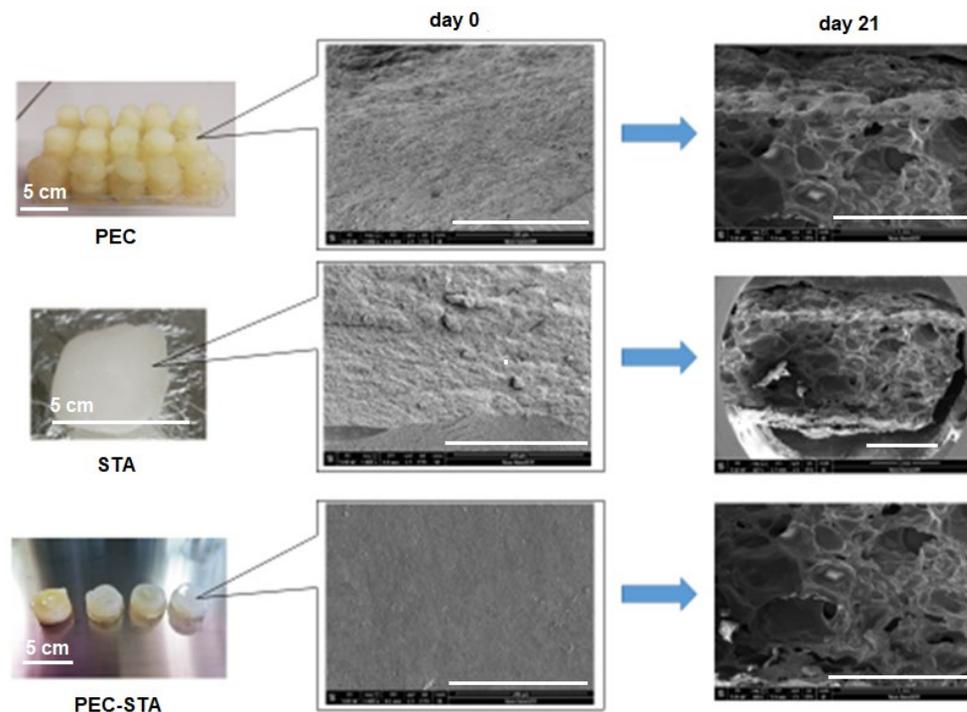


Figure 8. Images of the hydrogel formulations based on PEC (pectin), STA (starch), and PEC–STA (pectin–starch). SEM images of the dried formulations at day 0 and after 21 days buried in soil. SEM images bar = 500 μ m.

It should be noted that the soil microflora population, together with environmental factors, has a direct impact on biodegradation, which means that the particular results may differ in other types of soil and experimental situations.

3.4. Retention Rate of Picloram in Sandy Soil

Picloram is a persistent herbicide used to control a variety of annual and perennial broadleaved herbs and woody species [54]. Picloram is slowly metabolized by soil microorganisms and undergoes photolysis when exposed to sun. Its half-life in soil depends on the type of soil and climate and can be from a few weeks to three years. Picloram has high soil mobility as it does not bind soil particles and can move to depth layers. The high mobility represents one of the drawbacks that cause the loss and spread of the herbicide in the soil, with the possibility to contaminate underground water. For such reasons, strategies to retain Picloram near the site of interest and minimize mobility are needed. Encapsulation of Picloram in carriers or the use of hydrogels in soil represent promising strategies to solve such issues, as demonstrated in various studies [55–57].

In Figure 9, the release trends and the elution diagrams referring to Picloram are reported. As can be seen, there is capacity of PEC, STA, and PEC–STA hydrogels to hold Picloram in sandy soil and decrease its mobility. As can be observed, Picloram was retained in soil containing the hydrogels in the following order: PEC–STA > PEC > STA. The Picloram levels were 810 ppm (54%) and 870 ppm (58%) for PEC and STA, respectively, and 580 ppm (38%) for the PEC–STA composite after 30 days. Hydrogels are important in the development of carriers for releasing or controlling the mobility of various molecules in soil, with the possibility to regulate the release rate and intensity. They permit minimizing the environmental impact of agrochemicals, and in particular herbicides, pesticides by reducing losses due to leaching, volatilization, and degradation, maintaining their biological efficacy [50]. The results in Figure 9 reflect the trends reported in similar studies in which polysaccharide-based hydrogels have been used as carriers for prolonged release, and they suggest the relevance of further investigating the possibility to use such hydrogels for release of agrochemicals but also to control their mobility within soil layers [58].

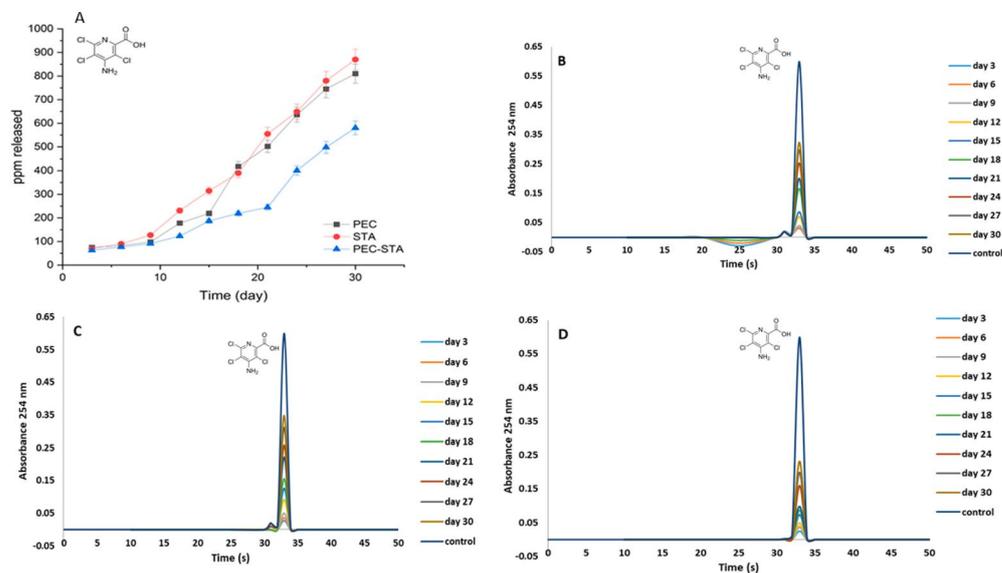


Figure 9. (A) Release trends of the herbicide Picloram from the PEC (pectin hydrogel), STA (starch hydrogel), and PEC-STA (pectin–starch hydrogel at 1:1 ratio). Elution diagrams of Picloram at different times referred to (B) PEC, (C) STA, and (D) PEC-STA.

The application of high-swelling water-insoluble crosslinked polymers as a soil amendment not only improves water consumption and fertilizer application efficiency through modifying the hydro-physical environment of soil [59,60] but also decreases runoff of pesticides and leaching losses due to their ability to modify soil physicochemical properties, including sorption behavior [61].

In this study, we did not analyze the potential molecular interaction between Picloram and the hydrogel structure because it was merely a preliminary attempt at testing

functionality. However, because of the encouraging preliminary results, it is important to investigate the possibility to reduce the leaching of other classes of agrochemicals and how to improve the hydrogels' performance.

4. Conclusions

The potential to create hydrogels using pectin and starch recovered from particular fruit wastes is demonstrated by the preliminary study's results. The produced hydrogels exhibit a high swelling capacity of up to 300% for a single component and about 400% for composite pectin–starch. A doubling in the time regarding water retention capacity compared to the control indicated the formulations' potential to promote moisture and water retention in sandy soil.

Because of the type and quantity of polysaccharides present, the hydrogels can break down naturally in soil at varying rates. The produced hydrogels can break down in soil, with the rate influenced by the type and amount of polysaccharides contained. After being buried in soil for 21 days, the biodegradation experiments show that the weight of STA hydrogels decreased by about 90%, PEC by 83%, and PEC–STA composite by just 60%. Pores of varying sizes and shapes were formed during bulk biodegradation, particularly in the interior section, as evidenced by a scanning electron microscopy analysis. The associated pore creation resulted in a nearly five-fold drop in the mechanical properties. By a possible alteration in Picloram's physical and chemical interactions with the soil, all the formulations show that it is possible to decrease the herbicide soil mobility by up to one month. The PEC–STA displayed the best performance. Further investigation into the application of these hydrogels to lessen pesticide mobility in soil is encouraged by the acquired results.

Although more research, particularly at the molecular level, is necessary to gain a deeper understanding of the mechanisms behind all the events reported, the current work is only at the preparatory stage. However, for the time being, we were interested in reporting a quick, straightforward, and inexpensive approach to processing food waste, at the laboratory scale, to generate materials with a great deal of opportunity to address the current call for more sustainable agriculture.

Author Contributions: Conceptualization, A.D.M., Y.W. and A.A.S.; methodology, A.D.M. and I.P.A.; validation, A.D.M.; formal analysis, A.D.M., A.I. and K.O.; investigation, A.D.M., A.I., K.O., I.P.A., A.D. and E.K.; resources, A.D.M., Y.W. and A.A.S.; data curation, A.D.M. and A.I.; writing—original draft preparation, A.D.M.; writing—review and editing, A.D.M.; supervision, A.D.M. and A.A.S. All authors have read and agreed to the published version of the manuscript.

Funding: The work was supported by the Ministry of Science and Higher Education of Russian Federation Nr 075-15-2023-602 (NIP TPU n 20.0060. MF.2023).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data available in a publicly accessible repository.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Majeed, A. Application of agrochemicals in agriculture: Benefits, risks and responsibility of stakeholders. *J. Food Sci. Toxicol.* **2018**, *2*, 3.
2. Jeschke, P. Pesticides and their use as agrochemicals. *Pest Manag. Sci.* **2015**, *72*, 210–225. [[CrossRef](#)] [[PubMed](#)]
3. Garrido, E.M.; Santos, M.; Silva, P.; Cagide, F.; Garrido, J.; Borges, F. Host-guest complexes of phenoxy alkyl acid herbicides and cyclodextrins. MCPA and β -cyclodextrin. *J. Environ. Sci. Health Part B* **2012**, *47*, 869–875. [[CrossRef](#)]
4. Işıklan, N. Controlled release study of carbaryl insecticide from calcium alginate and nickel alginate hydrogel beads. *J. Appl. Polym. Sci.* **2007**, *105*, 718–725. [[CrossRef](#)]
5. Tay, J.-W.; Choe, D.-H.; Mulchandani, A.; Rust, M.K. Hydrogels: From Controlled Release to a New Bait Delivery for Insect Pest Management. *J. Econ. Entomol.* **2020**, *113*, 2061–2068. [[CrossRef](#)] [[PubMed](#)]
6. Patra, S.K.; Poddar, R.; Brestic, M.; Acharjee, P.U.; Bhattacharya, P.; Sengupta, S.; Pal, P.; Bam, N.; Biswas, B.; Barek, V.; et al. Prospects of Hydrogels in Agriculture for Enhancing Crop and Water Productivity under Water Deficit Condition. *Int. J. Polym. Sci.* **2022**, *2022*, 4914836. [[CrossRef](#)]

7. Nikiema, J.; Mateo-Sagasta, J.; Asiedu, Z.; Saad, D.; Lamizana, B. *Water Pollution by Plastics and Microplastics: A Review of Technical Solutions from Source to Sea*; United Nations Environment Programme: Nairobi, Kenya, 2020.
8. Qamruzzaman; Ahmed, F.; Mondal, I.H. An Overview on Starch-Based Sustainable Hydrogels: Potential Applications and Aspects. *J. Polym. Environ.* **2021**, *30*, 19–50. [[CrossRef](#)]
9. Di Martino, A.; Khan, Y.A.; Durpekova, S.; Sedlarik, V.; Elich, O.; Cechmankova, J. Ecofriendly renewable hydrogels based on whey protein and for slow release of fertilizers and soil conditioning. *J. Clean. Prod.* **2021**, *285*, 124848. [[CrossRef](#)]
10. Khan, Y.A.; Ozaltin, K.; Bernal-Ballen, A.; Di Martino, A. Chitosan-alginate hydrogels for simultaneous and sustained releases of ciprofloxacin, amoxicillin and vancomycin for combination therapy. *J. Drug Deliv. Sci. Technol.* **2020**, *61*, 102126. [[CrossRef](#)]
11. Thombare, N.; Mishra, S.; Shinde, R.; Siddiqui, M.Z.; Jha, U. Guar gum based hydrogel as controlled micronutrient delivery system: Mechanism and kinetics of boron release for agricultural applications. *Biopolymers* **2021**, *112*, e23418. [[CrossRef](#)]
12. Thombare, N.; Jha, U.; Mishra, S.; Siddiqui, M.Z. Guar gum as a promising starting material for diverse applications: A review. *Int. J. Biol. Macromol.* **2016**, *88*, 361–372. [[CrossRef](#)]
13. Rosseto, M.; Krein, D.D.; Balbé, N.P.; Dettmer, A. Starch–gelatin film as an alternative to the use of plastics in agriculture: A review. *J. Sci. Food Agric.* **2019**, *99*, 6671–6679. [[CrossRef](#)] [[PubMed](#)]
14. Vinti, G.; Vaccari, M. Solid Waste Management in Rural Communities of Developing Countries: An Overview of Challenges and Opportunities. *Clean Technol.* **2022**, *4*, 1138–1151. [[CrossRef](#)]
15. Masoud, M.R.; Masry, E.; Fatma, H.; Hareedy, L.A. Utilization of Orange Wastes for Production of Value Added Products. *Egypt. J. Agric. Res.* **2017**, *95*, 221–231. [[CrossRef](#)]
16. Babalola, B.A.; Akinwande, A.I.; Gboyega, A.E.; Otunba, A.A. Extraction, purification and characterization of papain cysteine-proteases from the leaves of *Carica papaya*. *Sci. Afr.* **2023**, *19*, e01538. [[CrossRef](#)]
17. Caló, E.; Khutoryanskiy, V.V. Biomedical applications of hydrogels: A review of patents and commercial products. *Eur. Polym. J.* **2015**, *65*, 252–267. [[CrossRef](#)]
18. Ishwarya, S.P.; Nisha, P. Advances and prospects in the food applications of pectin hydrogels. *Crit. Rev. Food Sci. Nutr.* **2022**, *62*, 4393–4417. [[CrossRef](#)]
19. Sajilata, M.G.; Singhal, R.S.; Kulkarni, P.R. Resistant starch—A review. *Compr. Rev. Food Sci. Food Saf.* **2006**, *5*, 1–17. [[CrossRef](#)]
20. Tester, R.F.; Karkalas, J.; Qi, X. Starch—Composition, fine structure and architecture. *J. Cereal Sci.* **2004**, *39*, 151–165. [[CrossRef](#)]
21. Wesslén, K.B.; Wesslén, B. Synthesis of amphiphilic amylose and starch derivatives. *Carbohydr. Polym.* **2002**, *47*, 303–311. [[CrossRef](#)]
22. Dragan, E.S.; Apopei, D.F. Synthesis and swelling behavior of pH-sensitive semi-interpenetrating polymer network composite hydrogels based on native and modified potatoes starch as potential sorbent for cationic dyes. *Chem. Eng. J.* **2011**, *178*, 252–263. [[CrossRef](#)]
23. Biduski, B.; da Silva, W.M.F.; Colussi, R.; Halal, S.L.d.M.E.; Lim, L.-T.; Dias, Á.R.G.; Zavareze, E.d.R. Starch hydrogels: The influence of the amylose content and gelatinization method. *Int. J. Biol. Macromol.* **2018**, *113*, 443–449. [[CrossRef](#)] [[PubMed](#)]
24. El-Aziz, G.H.A.; Ibrahim, A.S.; Fahmy, A.H. Using Environmentally Friendly Hydrogels to Alleviate the Negative Impact of Drought on Plant. *Open J. Appl. Sci.* **2022**, *12*, 111–133. [[CrossRef](#)]
25. Yoshimura, T.; Sengoku, K.; Fujioka, R. Pectin-based superabsorbent hydrogels crosslinked by some chemicals: Synthesis and characterization. *Polym. Bull.* **2005**, *55*, 123–129. [[CrossRef](#)]
26. Konstantakos, S.; Marinopoulou, A.; Papaemmanouil, S.; Emmanouilidou, M.; Karamalaki, M.; Kolothas, E.; Saridou, E.; Papastergiadis, E.; Karageorgiou, V. Preparation of model starch complex hydrogels. *Food Hydrocolloids* **2019**, *96*, 365–372. [[CrossRef](#)]
27. Cury, B.; Klein, S.; Evangelista, R. Modeling a system of phosphated cross-linked high amylose for controlled drug release. Part 1: Synthesis and polymer characterization. *React. Funct. Polym.* **2008**, *68*, 1200–1206. [[CrossRef](#)]
28. Markov, P.A.; Khramova, D.S.; Shumikhin, K.V.; Nikitina, I.R.; Belosero, V.S.; Martinson, E.A.; Litvinets, S.G.; Popov, S.V. Mechanical properties of the pectin hydrogels and inflammation response to their subcutaneous implantation. *J. Biomed. Mater. Res. Part A* **2019**, *107*, 2088–2098. [[CrossRef](#)]
29. Santos, E.E.; Amaro, R.C.; Bustamante, C.C.C.; Guerra, M.H.A.; Soares, L.C.; Froes, R.E.S. Extraction of pectin from agroindustrial residue with an ecofriendly solvent: Use of FTIR and chemometrics to differentiate pectins according to degree of methyl esterification. *Food Hydrocoll.* **2020**, *107*, 105921. [[CrossRef](#)]
30. Sringam, J.; Pankongadisak, P.; Trongsatitkul, T.; Suppakarn, N. Improving Mechanical Properties of Starch-Based Hydrogels Using Double Network Strategy. *Polymers* **2022**, *14*, 3552. [[CrossRef](#)]
31. Koziół, A.; Środa-Pomianek, K.; Górniak, A.; Wikiera, A.; Cyprych, K.; Malik, M. Structural Determination of Pectins by Spectroscopy Methods. *Coatings* **2022**, *12*, 546. [[CrossRef](#)]
32. Marco-Brown, J.L.; Undabeytia, T.; Torres Sanchez, R.M.; dos Santos Afonso, M. Slow-release formulations of the herbicide picloram by using Fe–Al pillared montmorillonite. *Environ. Sci. Pollut. Res.* **2017**, *24*, 10410–10420. [[CrossRef](#)] [[PubMed](#)]
33. Shirbin, S.J.; Karimi, F.; Chan, N.J.-A.; Heath, D.E.; Qiao, G.G. Macroporous Hydrogels Composed Entirely of Synthetic Polypeptides: Biocompatible and Enzyme Biodegradable 3D Cellular Scaffolds. *Biomacromolecules* **2016**, *17*, 2981–2991. [[CrossRef](#)] [[PubMed](#)]
34. Krzyszowska, A.J.; Vance, G.F. Solid-Phase Extraction of Dicamba and Picloram from Water and Soil Samples for HPLC Analysis. *J. Agric. Food Chem.* **1994**, *42*, 1693–1696. [[CrossRef](#)]
35. Müller-Maatsch, J.; Bencivenni, M.; Caligiani, A.; Tedeschi, T.; Bruggeman, G.; Bosch, M.; Petrusan, J.; Van Droogenbroeck, B.; Elst, K.; Sforza, S. Pectin content and composition from different food waste streams. *Food Chem.* **2016**, *201*, 37–45. [[CrossRef](#)] [[PubMed](#)]

36. Twinomuhwezi, H.; Godswill, A.C.; Kahunde, D. Extraction and Characterization of Pectin from Orange (*Citrus sinensis*), Lemon (*Citrus limon*) and Tangerine (*Citrus tangerina*). *Am. J. Phys. Sci.* **2020**, *1*, 17–30. [[CrossRef](#)]
37. Wang, P.; Fei, P.; Zhou, C.; Hong, P. Stearic acid esterified pectin: Preparation, characterization, and application in edible hydrophobic pectin/chitosan composite films. *Int. J. Biol. Macromol.* **2021**, *186*, 528–534. [[CrossRef](#)] [[PubMed](#)]
38. Thanyapanich, N.; Jimtaisong, A.; Rawdkuen, S. Functional properties of banana starch (*Musa* spp.) and its utilization in cosmetics. *Molecules* **2021**, *26*, 3637. [[CrossRef](#)]
39. Berradi, A.; Aziz, F.; El Achaby, M.; Ouazzani, N.; Mandi, L. A Comprehensive Review of Polysaccharide-Based Hydrogels as Promising Biomaterials. *Polymers* **2023**, *15*, 2908. [[CrossRef](#)]
40. Wei, Y.; Durian, D.J. Rain water transport and storage in a model sandy soil with hydrogel particle additives. *Eur. Phys. J. E* **2014**, *37*, 97. [[CrossRef](#)]
41. Han, B.; Benner, S.G.; Flores, A.N. Evaluating impacts of climate change on future water scarcity in an intensively managed semi-arid region using a coupled model of biophysical processes and water rights. *Hydrol. Earth Syst. Sci. Discuss.* **2018**, 1–53. [[CrossRef](#)]
42. Choudhary, M.; Shalaby, A.; Al-Omran, A. Water holding capacity and evaporation of calcareous soils as affected by four synthetic polymers. *Commun. Soil Sci. Plant Anal.* **1995**, *26*, 2205–2215. [[CrossRef](#)]
43. Kumar, R.; Yadav, S.; Singh, V.; Kumar, M.; Kumar, M. Hydrogel and its effect on soil moisture status and plant growth: A review. *J. Pharmacogn. Phytochem.* **2020**, *9*, 1746–1753.
44. Laxmi, S.; Chanu, P.H.; Rani, P.; Rai, S.; Prasad, S.K.; Singh, R.K. Effect of hydrogel on soil moisture stress. *J. Pharmacogn. Phytochem.* **2019**, *8*, 316–320.
45. Tanan, W.; Panichpakdee, J.; Saengsuwan, S. Novel biodegradable hydrogel based on natural polymers: Synthesis, characterization, swelling/reswelling and biodegradability. *Eur. Polym. J.* **2018**, *112*, 678–687. [[CrossRef](#)]
46. Durpekova, S.; Di Martino, A.; Dusankova, M.; Drohsler, P.; Sedlarik, V. Biopolymer Hydrogel Based on Acid Whey and Cellulose Derivatives for Enhancement Water Retention Capacity of Soil and Slow Release of Fertilizers. *Polymers* **2021**, *13*, 3274. [[CrossRef](#)] [[PubMed](#)]
47. Wolf, P.; Reimer, M.; Maier, M.; Zollfrank, C. Biodegradation of polysaccharides, polyesters and proteins in soil based on the determination of produced carbon dioxide. *Polym. Degrad. Stab.* **2023**, *217*, 110538. [[CrossRef](#)]
48. Cheshire, M.V.; Greaves, M.P.; Mundie, C.M. Decomposition of soil polysaccharide. *Eur. J. Soil Sci.* **1974**, *25*, 483–498. [[CrossRef](#)]
49. Klein, M.; Poverenov, E. Natural biopolymer-based hydrogels for use in food and agriculture. *J. Sci. Food Agric.* **2020**, *100*, 2337–2347. [[CrossRef](#)]
50. Zamir, S.S.; Fathi, B.; Aji, A.; Robert, M.; Elkoun, S. Biodegradation of modified starch/poly lactic acid nanocomposite in soil. *Polym. Degrad. Stab.* **2022**, *199*, 109902. [[CrossRef](#)]
51. Khattab, A.M. The microbial degradation of pectin. In *Pectins: The New-Old Polysaccharides*; IntechOpen: London, UK, 2022; pp. 83–108.
52. Martin, J.P.; Haider, K.; Kassim, G. Biodegradation and stabilization after 2 years of specific crop, lignin, and polysaccharide carbons in soils. *Soil Sci. Soc. Am. J.* **1980**, *44*, 1250–1255. [[CrossRef](#)]
53. Luo, Z.; Zhang, Q.; Shi, M.; Zhang, Y.; Tao, W.; Li, M. Effect of Pore Size on the Biodegradation Rate of Silk Fibroin Scaffolds. *Adv. Mater. Sci. Eng.* **2015**, *2015*, 315397. [[CrossRef](#)]
54. Dumancas, G.G.; Rodney, T.L., Jr.; Subong BJ, J.; Koralege RS, H.; Perera UD, N.; Pham-Bugayong, P.J.; Cobbinah, E. *Picloram*; Elsevier: Amsterdam, The Netherlands, 2023.
55. Tomadoni, B.; Casalengué, C.; Alvarez, V.A. Biopolymer-based hydrogels for agriculture applications: Swelling behavior and slow release of agrochemicals. In *Polymers for Agri-Food Applications*; Springer: Berlin/Heidelberg, Germany, 2019; pp. 99–125.
56. Pang, L.; Gao, Z.; Feng, H.; Wang, S.; Wang, Q. Cellulose based materials for controlled release formulations of agrochemicals: A review of modifications and applications. *J. Control. Release* **2019**, *316*, 105–115. [[CrossRef](#)] [[PubMed](#)]
57. Khan, E.; Ozaltin, K.; Bernal-Ballen, A.; Di Martino, A. Renewable Mixed Hydrogels Based on Polysaccharide and Protein for Release of Agrochemicals and Soil Conditioning. *Sustainability* **2021**, *13*, 10439. [[CrossRef](#)]
58. Supare, K.; Mahanwar, P. Starch-Chitosan Hydrogels for the Controlled-Release of Herbicide in Agricultural Applications: A Study on the Effect of the Concentration of Raw Materials and Crosslinkers. *J. Polym. Environ.* **2022**, *30*, 2448–2461. [[CrossRef](#)]
59. Sarkar, D.J.; Singha, A.; Singh, N.; Parmar, B.S.; Kumar, A. Effect of Addition of Superabsorbent Hydrogels on Sorption and Mobility of Metribuzin in Sandyloam Soil. *Pestic. Res. J.* **2012**, *24*, 138–143.
60. Agaba, H.; Orikiriza, L.J.B.; Esegu, J.F.O.; Obua, J.; Kabasa, D.J.; Hüttermann, A. Effects of hydrogel amendment on plant accessible water and tree life under drought conditions. *Clean-Soil Air Water* **2010**, *38*, 328–335. [[CrossRef](#)]
61. Zhang, S.; He, F.; Fang, X.; Zhao, X.; Liu, Y.; Yu, G.; Zhou, Y.; Feng, Y.; Li, J. Enhancing soil aggregation and acetamiprid adsorption by ecofriendly polysaccharides hydrogel based on Ca²⁺-amphiphilic sodium alginate. *J. Environ. Sci.* **2022**, *113*, 55–63. [[CrossRef](#)]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.