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Suitability of Porous Inorganic Materials from Industrial Residues and Bioproducts for Use in Horticulture: A Multidisciplinary Approach

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Abstract: This study follows a circular economy approach through the preliminary implementation of a coated porous inorganic material (PIM), studied as sustainable controlled release fertilizer, and its application for lettuce Lactuca sativa L. cultivar Chiara growth. The PIM was made of pumice scraps that partially replaced clay as a natural raw material, spent coffee grounds as a porous agent, bovine bone ash and potassium carbonate to provide phosphorus (P) and potassium (K) nutrients, respectively. A coating made with defatted black soldier fly prepupae biomass was used as a nitrogen (N) source. Most of the ingredients used were industrial residues, with the aim of valorizing the raw waste materials present locally. The suitability of PIMs as a fertilizer was investigated with an interdisciplinary approach, which included the first chemical and physical characterization of the material, the evaluation of its antibacterial properties and of its use in horticulture through lettuce growth tests. As tests were carried out indoors, a specific LED lighting device was used to grow the lettuce. The release of nutrients into the soil was estimated by measuring the main elements in the fertilizers before and after their use in the soil. The first results from this characterization study support PIMs' suitability for agronomic applications. The use of the PIMs suggested average higher dry weight (49%), fresh weight (112%), and leaf area (48%), compared to those with the use of a standard fertilizer soil, without the release of any dangerous element for the plant in the soil. These results are a promising beginning for the development of further studies already in progress on sustainable controlled-release fertilizers.

Keywords: controlled-release fertilizers; lettuce; nutrients; LED; indoor horticulture; black soldier fly prepupae; circular economy

1. Introduction

Porous materials of inorganic, organic, or hybrid inorganic-organic origin find application in different fields thanks to their ability to interact with different species (atoms, ions, molecules) through their capacity for ion exchange, adsorption, and catalysis. Another significant application of this solid matrix with interconnected pores is within building energy technologies for energy conversion and storage purpose [1]: adsorption systems, thermal energy saving systems, insulation systems, evaporation systems, and geothermal systems [2]. In this context, green infrastructures such as green roofs or vertical forests can be seen not only from an aesthetic point of view but mainly as one of the most effective tools for adapting to climate change. The Mediterranean region is particularly involved in this issue as it is deeply affected by the desertification process, which leads to ecological degradation with the loss of soil production potential [3]. This, together with the quantitative and qualitative scarcity of water resources, prevents a rapid restoration of the vegetation cover of the soil [4]. The use of the green roof is a very popular solution also in Italy, and the reason is mainly due to two factors: constructive innovation and eco-sustainability. The green roof is a multilayer material consisting of six layers: waterproofing membrane, root barrier, drainage layer with optional water retention layer, filter cloth, growing medium, and plants. The drainage layer can be made up of organic or inorganic components. The former are polyethylene or polystyrene panels with holes to store more water during the drainage process. The latter are aggregates of lightweight expanded clay (LECA), expanded shale, crushed bricks, coarse gravel, and stone chips, which are granular draining materials with large pore spaces to store more water. A lightweight component can also be useful in indoor and outdoor home cultivation (with the use of ornamental and flowering plants, fruit trees, and horticultural species), employing hydroponic solutions or other gardening practices. In this way, it is possible to create real vegetable gardens to be installed in the house, on the roof, on the terraces or on the balconies. These "green solutions" are now expanding in the face of issues such as climate change, pandemics, and the need to increase the productivity of surrounding areas. The prospects of this type of materials could be improved if their properties such as lightness, porosity, water absorption, pH values, and electrical conductivity were combined with the ability to release nutrients, fertilizers, bioactive molecules, and other compounds with beneficial effects on plant growth, including antibacterial action [5].

In the context of circular economy and circular engineering, two phases of the change in the waste management paradigm and two compositions of porous inorganic materials (PIMs) were selected from a range of compositions previously tailored by the authors [6]. The contribution of silico-aluminate and silicate was provided by clay, as a natural raw material, and by the scraps from the extraction of pumice, the latter transformed in the form of both ceramic and glass matrix. The spent coffee grounds (SCGs) acted as poring agent. Bovine bone flour ash and K_2CO_3 were used, respectively, as sources for phosphorus and potassium. Nitrogen was added through an organic coating, based on defatted biomass from black soldier fly (BSF) prepupae. Bioconversion through insects using manure or other types of organic waste/byproducts as a rearing substrate is a much more sustainable alternative to manage this waste and reduce GHG emissions [7–9]. Insect biomass, in fact, provides high-value products (proteins, lipids, chitin) useful for many industrial purposes, and their frass is also used as a valuable crop fertilizer [10,11]. Finally, PIMs were used in growth tests to verify their potential as fertilizers.

This work is the first attempt to demonstrate the feasibility of growing a crop (baby lettuce *Lactuca sativa* L. cultivar Chiara) indoors by integrating new technologies to valorize local industrial waste while reducing the exploitation of natural raw materials using a multidisciplinary approach in a circular economy perspective.

2. Materials and Methods

2.1. Porous Inorganic Materials Formulations and Characterization

The core of the porous inorganic materials (PIMs) was realized using Red Clay sieved below 1 mm from a clay pit in the province of Modena (Italy) and pumice in the form of quarry scraps provided by Europomice Srl (Milan, Italy) with d < 100 μm at 1:1 rate. The first study conducted by Piccolo et al. [12] demonstrated the feasibility of making PIMs with pumice scraps only with high porosity results, therefore, a mixed clay and pumice formulation was tested in this study. Spent coffee grounds collected from coffee bars of Modena, dried and ground to 1 mm, are a post-consumer waste and were used as a porous agent (15 wt%) following the results of previous studies [13]. Potassium and phosphorus were added to the formulation using, respectively, potassium carbonate (K_2CO_3) and cattle bone flour ash originated from the calcination of the flour (900 °C). The nutrients were used as they were (formulation APNUT) and in a fertilizer glass (formulation APV50) as 50 wt% of the core's elements. Vitrification has the benefit of providing a controlled release of nutrients, preventing their waste, leaching in the soil, and the consequent underground water contamination. For this reason, studies and applications of fertilizer glass have been growing in the last few years [14].

The vitrifying agent chosen was pumice scraps, since the chemical and mineralogical analysis showed the basic constituents to form a glassy matrix, as melting components (Table 1), and a high amorphous fraction (79.7 wt%). The main crystalline phases of pumice instead were quartz (1.1 wt%), sanidine (11.2 wt%), and anorthite (3.0 wt%). Fertilizer glass (FG) was obtained in a color factory mixing all the components in a rotatory mill to obtain a homogeneous glass containing P_2O_5 = 18%; K_2O = 18%, SiO_2/Al_2O_3 = 3, and $K_2O + Na_2O$ = 20%. The mixture was melted in an electric industrial kiln at 1200 °C. In this study, pumice was also added to nonvitrified samples. The flash firing of the granules at 1000 °C simulated in fact the glass melting process and could give similar behavior and controlled release of nutrients of the vitrified fertilizer but with lower energy consumption.

Table 1. Chemical analysis (expressed in wt% oxides) with loss on ignition (L.o.I) and pH value of pumice scraps.

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	P_2O_5	Mn_3O_4	ZrO_2	SO_3	pH	L.o.I
56.6	18.6	3.94	0.54	3.06	1.17	1.98	8.55	0.13	0.13	0.07	0.13	7–8	4.84

Components were mixed manually adding distilled water to obtain a workable paste and then pelletized to form spheres with a diameter of 1–2 cm. The samples were then dried for 24 h at 105 ± 5 °C to remove free water and to avoid the formation of cracks during the thermal treatment. Finally, PIMs were fired in a static oven for 1 h at 1000 °C to simulate the thermal shock of expanded aggregates in the industrial kiln, obtaining a porous ceramic matrix for the combustion of the organic compounds. Both formulations were analyzed for physical and chemical properties to confirm the possible application in the agricultural field as controlled-release fertilizers.

The samples were weighed after the drying process (*Wi*) and after the firing (*Wf*) to measure the weight loss percentage (*WL* (%)) as the first information of the stability of the matrix and loss of organic compounds. The formula is:

$$WL(\%) = \frac{Wi - Wf}{Wi} \times 100 \quad (1)$$

Static water absorption percentage (*WA*24 (%)) was calculated by dipping 10 PIMs in distilled water for 24 h, following the standard procedure UNI EN 772-21:2011 [15]. The absorption capacity represents a fundamental characteristic for the application in gardening. It is strictly connected to the open porosity of the material. The formula is:

$$WA24(\%) = \frac{Ww - Wd}{Wd} \times 100 \quad (2)$$

where *Ww* is the weight of the wet samples after 24 h in distilled water and *Wd* is the initial dry weight of the samples.

PIMs used in soil must also guarantee good drainage capacity to release the absorbed water gradually over time, avoiding its excessive stagnation in the ground. Desorption capacity was therefore measured after the end of the 24 h absorption test, removing from the water and weighing the samples periodically after 30, 60, 120, 240, 480 min and after 24 h. For the measurements, the inorganic materials were in the condition of saturated surface dry (SSD), defined as the condition in which the surface of the particles is "dry", but the internal voids are saturated with water.

Total porosity was calculated from the analysis of loose bulk density (ρbulk) measured with Enveloped Density Micrometrics Geopyc 1360 Norcross, GA 30093, USA, and true density (ρreal) using a Helium Pycnometer (Micromeritics AccyPy1330, Micromeritic, Norcross, GA 30093, USA) with the formula:

$$TP(\%) = \frac{\rho \mathrm{real} - \rho \mathrm{bulk}}{\rho \mathrm{real}} \times 100 \quad (3)$$

pH (Digital pHmeter mod. PH6, XS/Eutech Carpi (MO), Italy) and electrical conductivity measures (EC) (Thermo Scientific Eutech Instruments, COND6, Breda, Holland) were performed following, respectively, UNI-EN 13037:2012 [16] and UN-EN 13038:2012 [17] standards for EC with a weight ratio of 1:5 between solid and distilled water. These parameters must be in the established limits (pH 6.5–7.5 and EC < 2 dS/m) to not damage the soil in which the fertilizers are applied or hinder the growth of plants [18]. Most horticultural crops, in fact, can have adequate growth in subacid, neutral, or sub-alkaline pH that represents the best conditions for nutrients' absorption. The soils with EC < 2 dS/m are indicated for every type of cultivation. The mineralogical composition of the samples was analyzed through X-ray diffraction using an automatic diffractometer X-Pert PRO, Panalytical (Malvern, UK), with Ni-filtered Cu Kα radiation, operating at 40 mA and 40 kV. For the qualitative analysis, the data were recorded in the 5–70° 2θ range. The spectra were analyzed using XPert High Score Plus software.

To complete the composition and to obtain a nitrogen, phosphorus, and potassium (NPK) fertilizer, an organic nitrogen-based coating was added to the PIMs, called APNUT_BSF and APV50_BSF. The coating was obtained using a bioproduct, i.e., the defatted biomass of black soldier fly (BSF) (*Hermetia illucens* L., Diptera: Stratiomyidae) prepupae, whose larvae had been reared on chicken manure [19], (51 wt%) mixed with glycerol (17 wt%) and water (32 wt%). The mixture was optimized using the Design of Experiment (DoE) approach deeply described in a previous study [20]. The BSF larvae had been reared in glass containers on an optimized mixture of poultry manure, water, and micronized chabazite [19] inside climatic chambers at 27 ± 0.5 °C, 80–90% relative humidity in dark conditions.

2.2. Antibacterial Activity of the Porous Inorganic Materials

Antibacterial properties become of primary importance for materials engineered for soil applications and which involve handling, storage, and use in confined environments (indoor cultivation). The antibacterial activity of the core (APNUT, APV50), of the coated samples (APNUT_BSF, APV50_BSF), and of the fertilizer glass (FG) were therefore analyzed and reported as bacterial viability (BV) (as % of cell reduction) of Gram-negative and positive assayed strains. In particular, *E. coli* and *P. aeruginosa* were evaluated as Gram-negative bacteria, while *S. aureus* and *E. faecalis* as Gram-positive strains. The antibacterial properties were evaluated following the entire procedure as reported elsewhere in [21]. The following equation reports the calculation of BV (%):

$$BV(\%) = \frac{Pd - Id}{Pd} \times 100 \quad (4)$$

where Pd is the Petri diameter and Id is the Inhibition halo diameter.

2.3. Germination and Plant Growth Test

The fertilizers obtained were tested on baby lettuce *Lactuca sativa* L. cultivar Chiara (ISI Sementi SpA, Fidenza, Italy), a vegetable specie of horticultural interest, chosen because of its short life cycle (3–4 weeks) and because its small size allows it to be grown both indoors and outdoors, in small pots or jars, vertical green walls, etc. The substrate used for the growth test was made by mixing agri-perlite Agrilit 3 (Perlite Italiana Srl, Italy) (particle size 2–5.6 mm, density 90 kg/m^3) with a peat moss soil, Potgrond H (Klasmann, Germany), pH 5.5, salinity 3.5 dS/m, containing N (210 mg N/L), P (150 mg P_2O_5/L), K (270 mg

K_2O/L), Mg (100 mg Mg/L) plus micronutrients. Agri-perlite and peat moss soil were mixed at a rate of 3:1, respectively, with the aim of reducing the use of substrates of natural origin, decreasing the environmental impact linked to the exploitation of peat. Five seeds of lettuce per pot (with a capacity of 500 mL) were placed on the potting medium, and a quantity of water (50 mL/pot) was provided every 3 days. Six coated fertilizer granules were added to each pot, placing them in two layers in the center of the substrate. Two pots had APNUT_BSF and two pots had APV50_BSF. Another 4 pots without PIMs (controls) were prepared. The pots were placed in a growth room at 21 ± 2 °C and relative humidity of 38 ± 7% for 21 days under artificial light and long-day conditions (16 h light, 8 h dark).

At the end of the 21 days, the following data were collected: average fresh weight/pot (g) of the plants, recorded as total fresh mass (TFM) and average dry weight/pot (g), recorded as total dry mass (TDM). The latter was obtained after drying the plants in a ventilated oven at 80 °C for 24 h. The average leaf area/pot (LA) was measured considering two plants for each pot and the three largest leaves of each plant. Prior to the measurement, the leaves were cut from the two plants and then scanned and analyzed using ImageJ software (version 1.52, NIH, Bethesda, MD, USA). The total area of the three leaves was considered for each plant, and the average value of the plant area for each pot was calculated.

2.4. Light Conditions

Artificial light conditions were created in the growth chamber by exploiting ad hoc light recipes made using a PHYTOFY® RL LED module from OSRAM (Munich, Germany), which is specifically designed for indoor horticulture applications allowing for fully tunable light spectra in terms of intensity per wavelength. The intensity associated with every wavelength is expressed as photosynthetic photon flux density (PPFD), thus, the portion of emitted photons that contributes to the photosynthesis in the photosynthetic active region (PAR) is constituted by wavelengths in the range 400–700 nm. The LED light recipe chosen for these preliminary growth tests is a standard composition summarized in Figure 1.

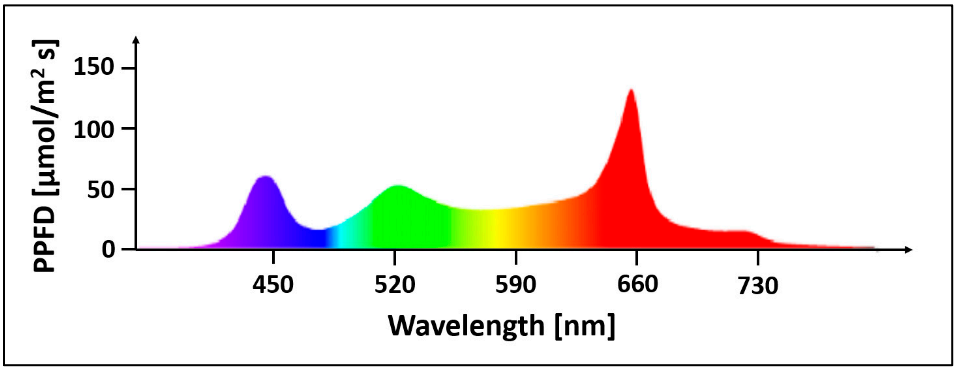

Figure 1. Graph of the light recipe used during growth tests for lettuce vegetative growth. The vertical axis displays the photosynthetic photon flux density (PPFD).

The PPFD emitted by the panels was approximately 212 µmol m^{-2} s^{-1} with a photoperiod of 16 h/day, equal to 12.15 mol m^{-2} d^{-1}. These technical data have also been confirmed by several studies carried out on lettuce growth where the use of white and green light has shown an improvement in the fresh mass of the plants [22], the combination of red and blue lights can favor lettuce growth, and the application of red/far red stimulates the germination process, also increasing light capture [23]. The distance of the LED panels from the plants was 75 cm, kept constant for the entire duration of the test. According to the layout and the chosen light recipe, the PPFD map of the area under the LED panel is exposed in Figure 2. The pots used for growth experiments were placed within the two active areas highlighted by the black rectangles. This allowed ensuring as uniform lighting conditions as possible for each lettuce plant.

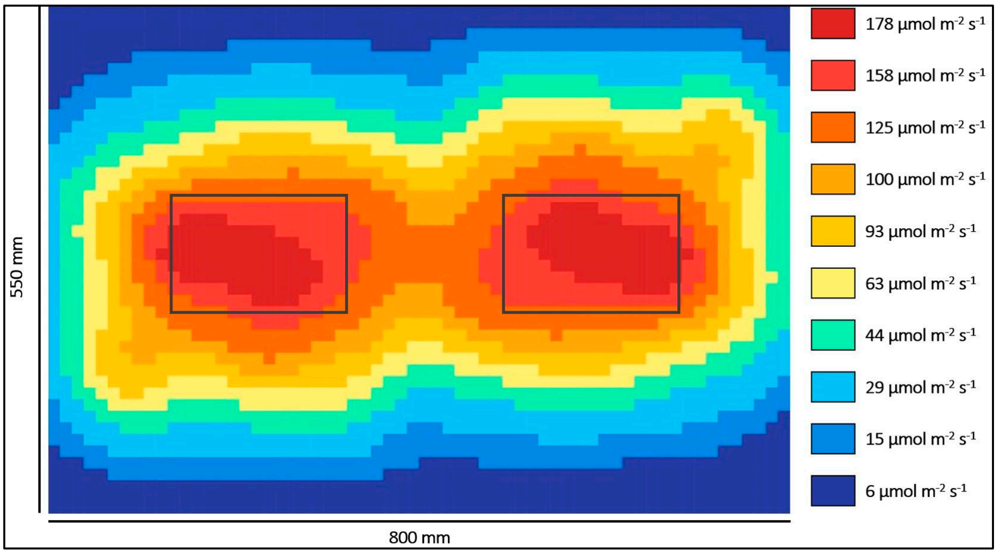

Figure 2. Estimated PPFD map under the LED module used for growth experiments, according to the producer's software at a distance of 75 cm between the pots and the LED module. The active area used for the growth experiments is indicated by the two black rectangles.

2.5. Release Tests on PIMs

To verify the amount of nutrients released by the fertilizers into the soil, the concentration of the elements in the coated PIMs was measured before and after the application in the soil. This type of analysis is not accurate enough to verify the real quantity of nutrients absorbed by the plant, but it can be a first screening of the behavior of APNUT_BSF and APV50_BSF in the soil as fertilizers. The analyzed elements were total N, exchangeable K, and assimilable P as the main nutrients, but also exchangeable magnesium as a secondary nutrient. The concentration of total N was measured through digestion, distillation, and titration according to UNI 10780:1998 (APP J.I.) [24], while for the measurement of exchangeable Mg and K, a release test in 1 N ammonium acetate was used according to D.M. 13/09/99 [25]. Assimilable phosphorus was measured as phosphate through a spectrophotometric method as indicated in D.M 13/09/99 [25]. Aluminum and lead have been checked as possible hazardous elements for the plant and measured using the method of attack in aqua regia followed by ICP (UNI EN16174:2013 [26] and UNI EN1670:2016 [27]). Data was also collected on pH measured at 20 °C, salinity at 25 °C (through a conductivity measurement), and humidity after drying the porous materials at 105 °C.

3. Results and Discussion

3.1. Characterization of PIMs

The physical characterization of APNUT and the APV50 matrix, reported in Table 2, showed a weight loss (WL (%)) similar for both formulations due to the evaporation of internal water, decomposition of organic compounds (SCG), and decomposition of carbonates during firing. The firing process therefore also influenced the total porosity (TP (%)) of the material and the water absorption capacity (WA24 (%)) even if nonvitrified PIMs had greater water absorption due to the absence of glass which inhibited the formation of pores, influencing the entrapment of nutrients and water in the core. The pH and EC respected legal limits for use in soils, with a slight increase in pH in the nonvitrified formulation. pH can be influenced by several factors. Spent coffee grounds, for example, have a neutral pH, therefore, it has been added in previous studies to neutralize the pH of PIMs that used other alkaline poring agents, such as biochar [28]. Fertilizer glass (FG), on the other hand, does not appear to affect the pH of PIMs, even though it has an alkaline pH [6]. The results obtained showed that the use of pumice scraps in the matrix instead of clay had a positive effect on the porosity of the granules, with values around 50% for

APV50, increasing the value as compared to the porosity of PIMs consisting only of clay (43%) reported by Andreola et al. [13]. This result also affected other properties such as water absorption, which went from 12% [13] to over 20% in pumice/clay PIMs.

Table 2. Characterization of granules with fertilizer glass (APV50) and with nutrients that were not vitrified (APNUT).

	WL (%)	Bulk Density (g/cm^3)	True Density (g/cm^3)	TP (%)	WA24 (%)	pH	EC (dS/m)
APNUT	14.46	1.146	2.6497	56.14	30.73	7.38	0.220
APV50	12.76	1.260	2.6523	51.88	22.0	6.60	0.268

The desorption capacity of the granules was measured after the absorption test (Figure 3). The progressive weight decrease was due to the release of water during the 24 h. The APV50 stabilized its weight after 8 h, and both samples returned to their initial dry weight, measured before the absorption test, in 24 h, as during this time they completely released the absorbed water. The lower absorption (22%) and desorption of water from APV50 compared to those of APNUT were due to the presence of the FG which, as already demonstrated, reduced the open porosity of the material.

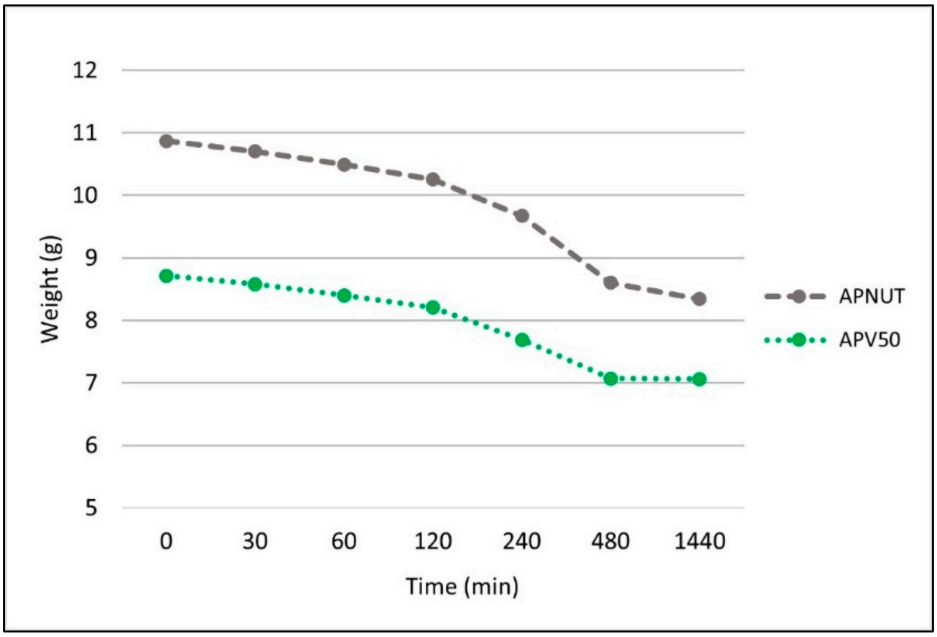

Figure 3. Water desorption from APNUT and APV50 in 24 h.

From the analysis of the mineralogical phases plotted in Figure 4a,b, the two core formulations showed identical crystalline phases, identifying quartz (SiO_2) as the main phase. The other three phases, on the other hand, could be attributed to the presence of the nutrients P and K (leucite: $KAlSi_2O_6$; sanidine: $KAlSi_3O_8$; hydroxyapatite: $Ca_5(PO_4)_3(OH)$). APV50 revealed a lower degree of crystallinity than APNUT did, probably due to the addition of the fertilizer glass, which increased the amorphous phase of the material.

The characterization of the two core formulations did not show significant differences in terms of physical and chemical properties between vitrified (APV50) and nonvitrified (APNUT). Therefore, both formulations could be used for agronomic applications, respecting the pH and EC limits for use in soils and demonstrating good draining capacity. The nutrients and pumice could potentially replace FG without compromising the final performance of the fertilizer. The use of nonvitrified nutrients can reduce the energy consumption given by the vitrification process, as demonstrated by the analysis of the carbon footprint [29], improving the sustainability of the final product. To confirm the comparable performance of the two formulations for nutrient delivery in the soils, a growth test was performed on lettuce.

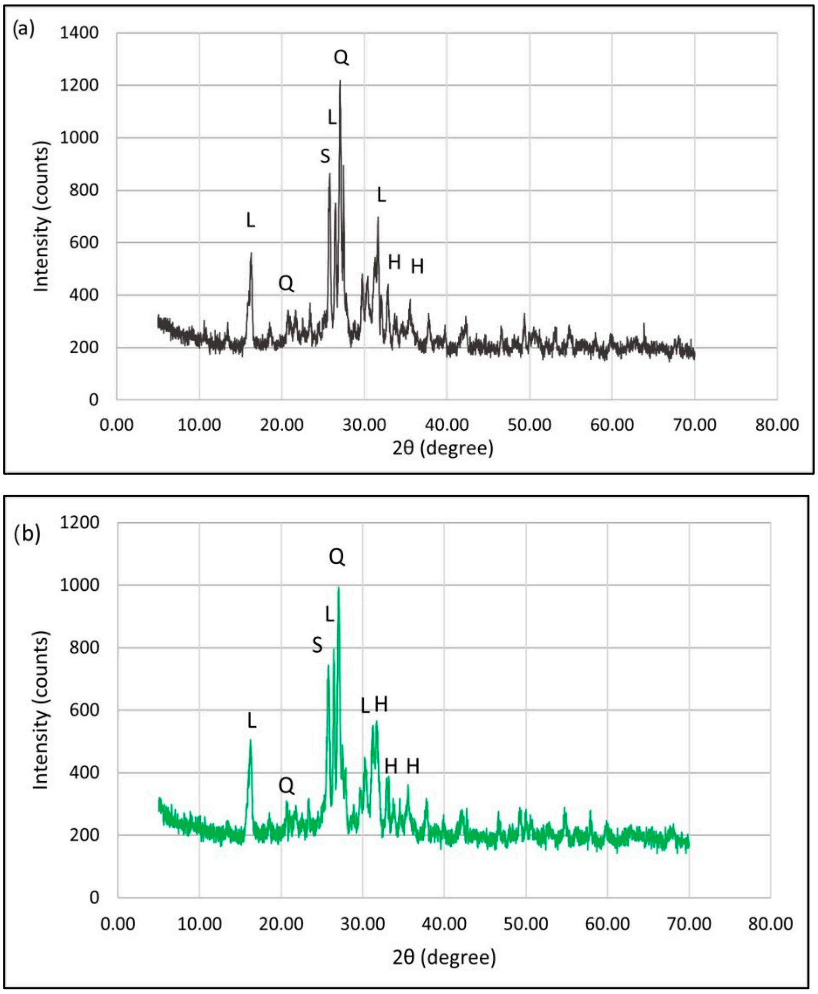

Figure 4. X-ray diffractograms of APNUT (**a**) and APV50 (**b**) (Q = quartz; L = leucite; S = sanidine; H = hydroxyapatite).

3.2. Antibacterial Activity

To shed light on the ability to inhibit microbial growth, four bacterial strains (*E. coli*, *P. aeruginosa*, *S. aureus*, and *E. faecalis*, respectively) were plated and incubated in the presence and absence of FG, APV50, APV50_BFS, APNUT, and APNUT_BFS. All the results are reported in Figure 5, which shows that there were no differences between the inhibition halos obtained in the presence of FG and those obtained in the presence of the synthesized materials, both with and without coating. Indeed, BV (74.67–82.88 %) values were very similar to each other. These values were lower than the values of the controls (BV = 100%) because there was no growth where the material was directly in contact with the bacteria plated on the solid media. The absence of inhibition halos around the sample powders could be explained by the inability of the materials to release toxic or high inhibitory organic/inorganic compounds that could adversely affect microbial growth.

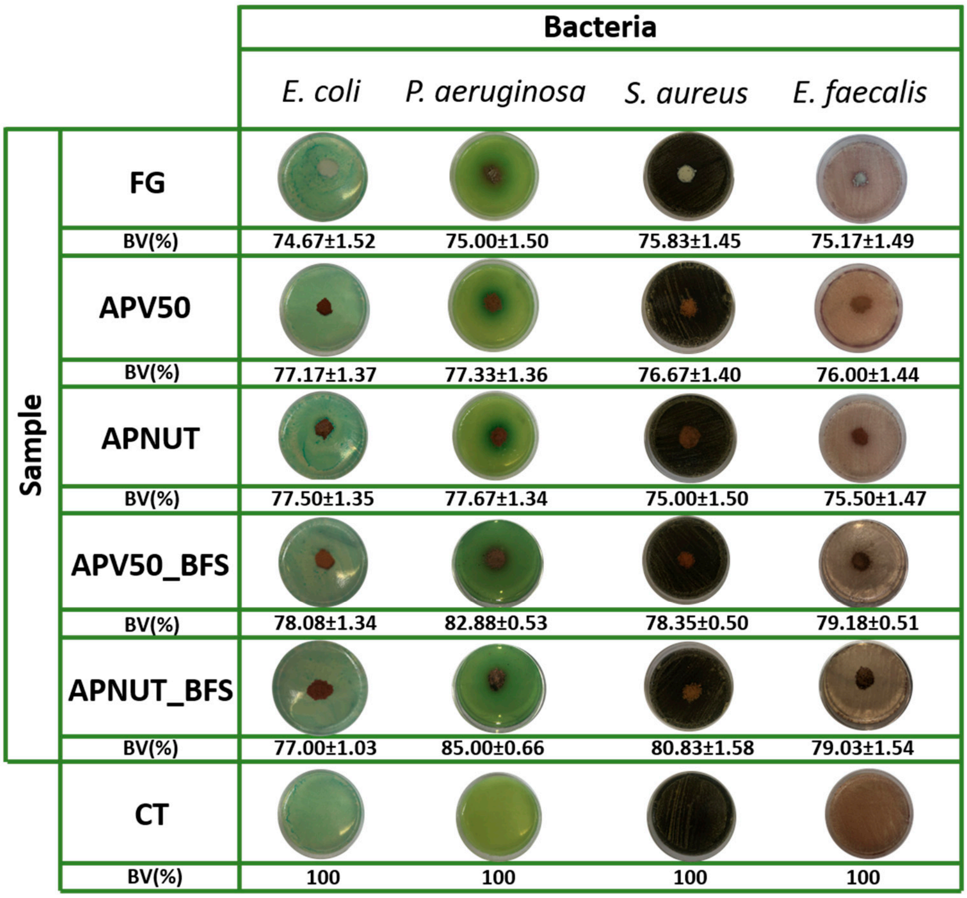

Figure 5. Bacterial viability (BV (%)) data and antibacterial assay figures. CT = control.

3.3. Lettuce Growth

The germination test, recorded within seven days of sowing, gave germination percentages between 80% on the control substrate and 95%, the latter obtained both on the substrate plus APNUT_BSF and plus APV50_BSF. In each pot, four to five lettuce plants were observed (Table 3), indicating that the climatic and soil conditions were adequate and favorable for the selected plant species. No visible symptoms of phytotoxicity were recognizable on the leaves. The plants obtained on the substrate with the two types of PIMs showed better results for all the parameters considered, compared to the plants growing on the control substrate. Figure 6 shows the results of the growth test, recorded after 21 days of cultivation. Plants grown on the substrate with fertilizer PIMs had higher fresh (TFM) and dry mass (TDM). An increase in fresh weight of lettuce of 47.6% with APV50_BSF and 50.8% with APNUT_BSF was observed, compared to lettuce grown on the control substrate. This suggests that the fertilizer PIMs could improve the growth of lettuce. The average dry weight of the plants increased instead to 112.4% and 125.7%, respectively, with the use of vitrified and nonvitrified fertilizer PIMs compared to that in the control test. Furthermore, a greater average leaf area (LA) was measured in lettuce plants grown on substrates with APV50_BSF (45.5%) and APNUT_BSF (50.4%) compared to that of those grown on the control one. These first results suggest that the use of fertilizer granules was relevant for obtaining larger plants with more biomass and larger leaves, using a substrate poor in natural soil. According to these first tests, no significant growth differences were observed when comparing the use of vitrified and nonvitrified fertilizers, although better results were obtained with APNUT_BSF for all the observed parameters. Therefore, the growth data suggest the interchangeability of the two PIMs formulations.

Table 3. Germination and growth values obtained growing lettuce in control condition (substrate without fertilizer) and with fertilizer APV and APNUT.

	Number of Plants/Pot (Average)	TFM (g)	TDM (g)	LA (mm^2)
Control	4	0.719	0.063	27.950
APV50_BSF	5	1.527	0.093	40.675
APNUT_BSF	4.5	1.623	0.095	42.025

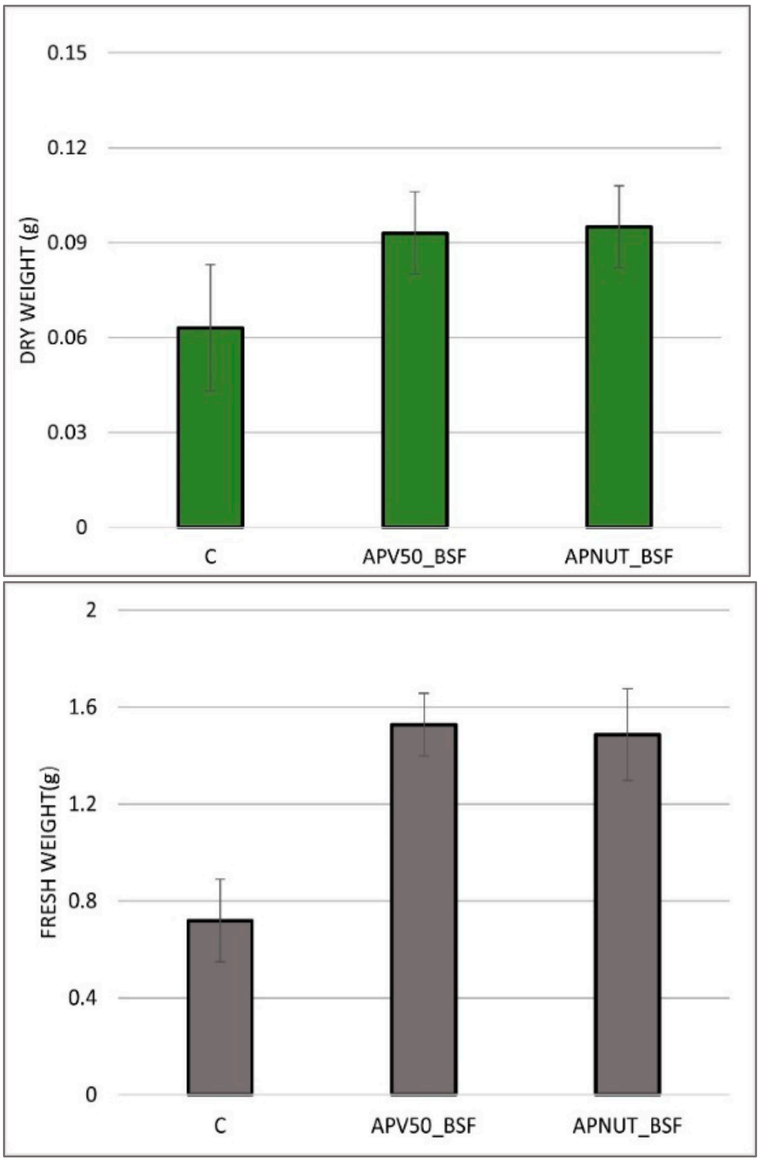

Figure 6. Lettuce biomass measured within 21 days of cultivation in pots with fertilizer APV50_BSF and APNUT_BSF and without fertilizer (C). The error bars represent the deviation standard calculated on the values measured.

3.4. Release of Nutrients

The chemical and physical properties of fertilizers have been investigated before and after their use in the soil. The results are shown in Table 4. The pH was generally neutral, and it did not change significantly after using the porous coated materials in the soil. Only APV50_BSF had a small increase to alkaline pH. pH analysis of the coated granules also suggested that the application of the organic coating did not affect the initial pH of the core analyzed (Table 2). These values are in the correct range to maximize the availability of nutrients, and the small increase of the pH was positive. This indicates that there was no overapplication of nutrients, which would cause soil acidification, and also indicates the potential of coated PIMs to improve pH in acidic soils [30]. The salinity in the granules decreased after use, demonstrating the release of ions into the soil during the test. Salinity is another parameter to be taken into consideration because excessive salinity can cause the plant to lose its ability to absorb nutrients. Despite the small difference, humidity was lower in APV50_BSF, suggesting that the addition of the fertilizer glass reduced the water absorption capacity of the matrix. Higher humidity is preferable, as the swelling ability of the fertilizer helps the soil retain water, allowing plants to grow for longer periods without the need to add water.

Table 4. Parameters of the granules (pH, salinity, humidity) before (APNUT_BSFnew, APV50_BSFnew) and after (APNUT_BSFused, APV50_BSFused) use in the soil for the lettuce growth test.

	pH (20 °C)	Salinity 25 °C (meq/100 d.b.)	Humidity (%)
APV50_BSFnew	6.8	14.5	5.8
APV50_BSFused	8.6	1.2	4.2
APNUT_BSFnew	6.6	13.9	6.2
APNUT_BSFused	7.2	5.7	8.8

From a first analysis of the main elements shown in Figure 7, it was possible to notice that after 21 days the amount of considered elements had decreased in PIMs, suggesting that the ions were released into the soil. The percentages of nutrients released showed some differences between APV50_BSF and APNUT_BSF fertilizers. The nitrogen (Figure 7a) present in the coating was released more in the nonvitrified granules with a 77% reduction from the unused fertilizer (APNUT_BSFnew). The release of nitrogen from APV50_BSF was instead 63%. Considering that the coating was the same for the two fertilizers, the different releases could be due to the different core. Indeed, APNUT showed greater porosity and water absorption (Table 2), which could lead to greater water exchange and nutrient release with the surrounding soil. However, the release of assimilable phosphorus, shown in Figure 7b, showed an opposite trend, as it decreased by 85% and 59% for APNUT_BSF and APV50_BSF, respectively. This could be due to the inclusion of phosphorus in the fertilizer glass as a network former, which would hinder its release [13,31]. Exchangeable potassium (Figure 7c) decreased by 90% in APV50_BSF and by 88% in APNUT_BSF, showing no differences among the two coated PIMs. The release of magnesium in the soil is another important parameter because it makes possible the synthesis of chlorophyll in plant leaves and is involved in some important enzymatic activities [32]. The release of this element was 64% from APNUT_BSF and 79% from APV50_BSF (Figure 7d). The main difference relates to the release of phosphorus and magnesium, suggesting that different PIMs should be used according to different nutritional needs.

These data are in agreement with the results obtained from germination and growth tests carried out with lettuce plants. The addition of APNUT_BSF and APV50_BSF seemed to improve both growth and size of the plant throughout the entire growing cycle. This would also make it possible to reduce the consumption of soil taken from the natural environment, limiting the use of natural resources.

Pb and Al can be dangerous elements for the soil and for this reason, it is important to know their quantity in fertilizers and their eventual release into the soil. An instrumental uncertainty equal to 20% for the measurements represented in Figure 8a,b, suggested that no significant variations in concentration were found between the new granules and the used ones. The presence of Pb in the coated PIMs was due to the vitrification process. In fact, the amount in APV50_BSF was significantly higher than that in in APNUT_BSF, as shown in Figure 8a. Pb is a heavy metal with hazardous effects on human health and the environment. For this reason, the World Health Organization (WHO) recommends a safe limit of Pb in soils used for agriculture under 100 ppm [33]. The constant amount of metal present in fertilizers before and after use in the soil suggests that they did not significantly release this element into the soil. Al is another toxic element for soils because root growth can be affected by an amount of Al > 400 ppm, preventing plants from accessing water and nutrients. Additionally, the concentration of this element in the tested fertilizers did not change by applying the coated PIMs in lettuce cultivation (Figure 8b), suggesting that it was not released into the soil. These results agree with the absence of any sign of injury on plants, even if it will be necessary to exclude phenomena of bioaccumulation in the plants. The results presented suggest that both fertilizers could have good performance in nutrient release while maintaining low content of potentially hazardous elements.

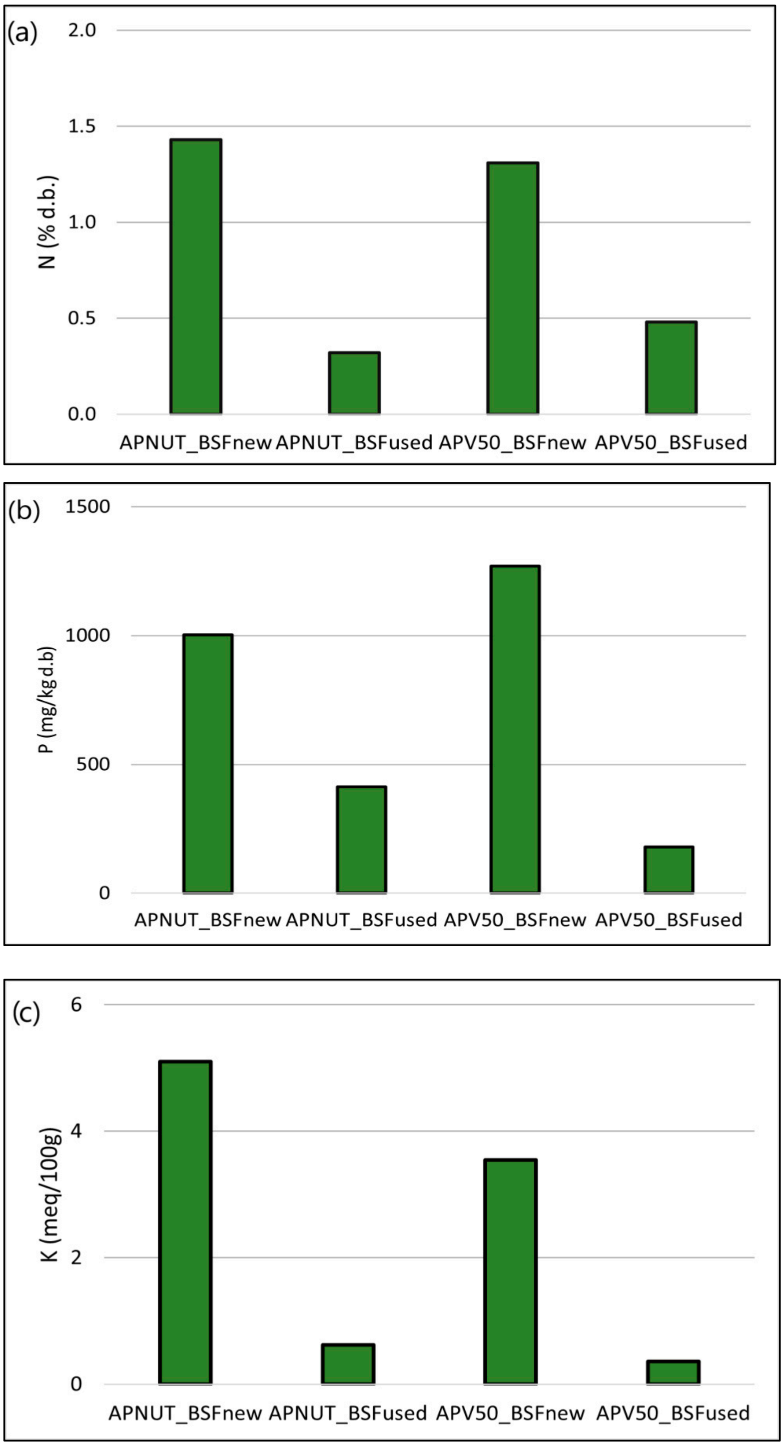

Figure 7. *Cont.*

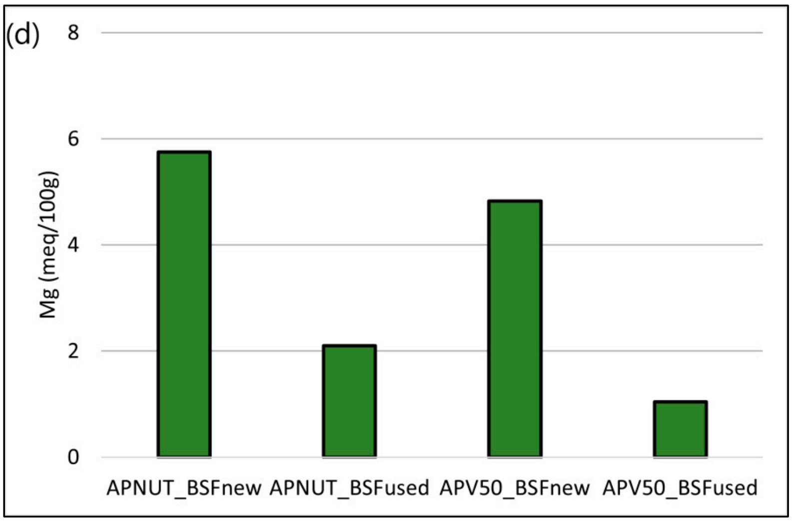

Figure 7. Concentrations of N (**a**), P (**b**), K (**c**), and Mg (**d**) in the coated PIMs before (APNUT_BSFnew, APV50_BSFnew) and after (APNUT_BSFused, APV50_BSFused) the use as fertilizers in the soil for 21 days. Instrumental uncertainty is equal to 20% of the values.

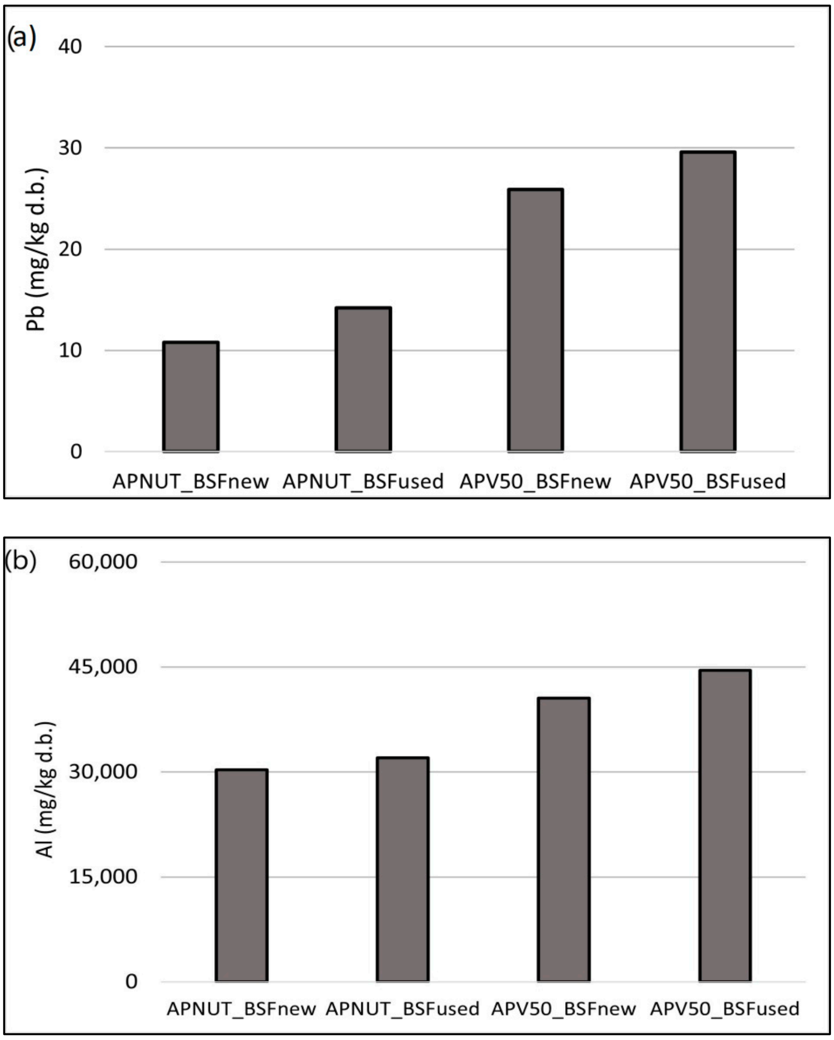

Figure 8. Pb (**a**) and Al (**b**) concentrations in the PIMs before (APNUT_BSFnew and APV50_BSFnew) and after (APNUT_BSFused, APV50_BSFused) their use as fertilizers in the soil. Instrumental uncertainty is equal to 20% of the values.

4. Conclusions

In this study, a new formulation of porous inorganic materials as a controlled-release fertilizer was characterized and preliminarily tested in the soil. The use of pumice scraps effectively increased the porosity and lightness of the PIMs, reducing the consumption of natural raw materials. The application of another industrial waste in the PIMs formulation, in addition to the spent coffee grounds and bovine bone ash, already tested in previous studies, increases the sustainability of this type of controlled-release fertilizers, according to the principles of circular economy promoted by European Union. Nutrients were added to the formulation both as separated materials and in a fertilizer glass. First results suggest that the two fertilizers showed similar properties, although the application of the vitrification process affected porosity and absorption capacity. The characterization of the PIMs also demonstrated the possibility of using them in the agricultural field for pH and EC values, measured according to the regulatory limits, while antibacterial analysis confirmed the possibility of safely handling the granules, which showed inert behavior even for the BSF-based coating. This aspect opens the possibility of extending the use of porous materials in a domestic context. Comparing lettuce growing in unfertilized soil and with the coated PIMs gave a preliminary indication that fertilizers could have a significant impact on biomass growth, measured as fresh and dry mass. The two formulations of PIMs, APNUT_BSF, and APV50_BSF appeared to contribute similarly, although APV50_BSF may have slower nutrient release due to fewer open pores. Finally, the first approach to verify the behavior of porous materials in terms of nutrient release was carried out with a chemical analysis of the nutrients contained in APNUT_BSF and APV50_BSF before and after 21 days of lettuce growth. The measured amount of nutrients in general decreased, suggesting that they were released into the soil and were made available to the plants, thus contributing to the growth of biomass, as confirmed by the morphological data and the weight of plants. The content of hazardous elements such as Pb and Al, on the other hand, did not change, and they were measured in small quantities in the PIMs, suggesting that they were not hazardous for agricultural application. This multidisciplinary preliminary study is therefore a positive start that encourages future research on fertilizers based on pumice scraps for crop growth in confined spaces. However, further confirmation is needed, and statistical validation of these preliminary results will be the object of future and more extended works.

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