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Preliminary Study on Sustainable NPK Slow-Release Fertilizers Based on Byproducts and Leftovers: A Design-of-Experiment Approach

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ABSTRACT: In this study, an organic nitrogen-based coating was developed based on black soldier fly (BSF) prepupae reared on poultry dejections and deposited on ceramic lightweight aggregates (LWAs), containing phosphorous (P) and potassium (K) from agroresidues, leading to a complete nitrogen, phosphorus, and potassium (NPK) fertilizer. To obtain a resistant coating with good adhesion to LWAs, different plasticizing agents were tested (e.g., glycerol, cellulose, and polyethylene glycol). The coating formulation was optimized through a design-of-experiment (DoE) approach to correlate the effect of each mixture component on the coating's performance. BSF biomass was characterized through chemical and thermal routes, as well as the final coated LWAs, confirming their general agreement to fertilizer's requirements. Release tests in static conditions highlighted the barrier action of the coating, preventing uncontrolled release of potassium and phosphorus contained in the LWAs as well as the release of nitrogen after 21 days (near to 20%). Germination and growth tests indicated a valuable increase of the growth index, whereas the germination process is limited by the coating barrier effect. This work proposes a new product in the field of slow-release fertilizers designed by rational methodologies and innovative materials based on waste valorization, fully in agreement with a circular economy perspective.

INTRODUCTION

The growth of the global economy since the 1970s of the twentieth century until today has led to a strong increase of resource and energy consumption as well as human population.[1] Since the economic—demographic forecasts for the future show a similar development, it is necessary to rethink production methods and find new ways to obtain raw materials in a sustainable way for environment preservation.[2−4] In this context, agriculture is an important sector, both from economic and demographic points of view, and efficient soil exploitation methods will become even more strategic in the next decades.[5]

Thereafter, advanced fertilizers, such as controlled-release fertilizers (CRFs), are mandatory in agriculture and their production criteria must take into account the more recent legislation about raw material exploitation.[6] CRFs are fertilizers that release an amount of nutrients not exceeding 75% of the total in the first 28 days of use at a temperature of 25 °C.[7] Thereby, the soil absorption of nutrients is optimized, and their dispersion in the environment, especially in groundwater, is strongly limited. A clear example of raw material exploitation to be taken into account for CRFs design is represented by phosphorus: it is essential for plant growth, but the worldwide availability of ores that can provide this element is decreasing, and for this reason, it is classified as a critical raw material by the European Union.[8] The use of CRFs also includes some drawbacks, such as a lack of correspondence between

laboratory and field tests, high production costs, difficulty in storage, and loss of compounds that can pollute the soil. In fact, the most common type of CRFs is characterized by a conventional fertilizer enclosed in a coating or dispersed in a matrix, able to regulate nutrient release, that mainly consists of petroleum-based plastic.[9,10] Therefore, the most recent research is following two directions: the first concerns the development of more efficient CRFs, able to improve nutrient assimilation of the cultivation, and the second aims to find new sustainable raw material sources for their formulation. The mechanism of controlled release is regulated first by the progressive degradation of the coating and second by the osmotic pressure inside the core; thereafter, high hydrophilic and environmentally green compounds must be considered to avoid the pollution of soil after coating degradation. In this sense, the more recent research is dedicated to the study of coating or matrix-based on natural materials, such as bentonite and cotton stalks,[11] lignin,[12] wheat straw,[13] chitosan and vegetal cellulose,[14] and chitosan and potato starch.[15] Studies so far demonstrated that the obtainment of a gradual controlled release over a period of 21 days is difficult because it is necessary to avoid too fast biodegradation of the coating due to very high hydrosolubility of the natural materials, and therefore, research must be focused on the need for greater control of the coating formulation.

In this context, the principal aim of the paper is to develop a sustainable coating based on organic biomass valorization from a circular economy perspective. In fact, in this study, black soldier fly (*Hermetia illucens*, BSF) biomass, naturally enriched in nitrogen, has been tested as the main component of coating-suitable CRFs, exploiting the ability of this insect to rear on a wide range of different types of substrates, including organic wastes, avoiding transmission of pathogenic agents.[16,17] The elemental composition of BSF prepupae changes depending on the type of the rearing substrate, but the high contents of proteins and chitin (near to 30 wt %) make them extremely attractive sources of nitrogen.[18−21] As far as the authors know, this is the first study that investigates this type of biomass as a possible component for CRF design.

In particular, chitin is a polysaccharide composed of a long-chain linear polymer, given by (1−4)-linked 2-acetamido-2-deoxy-β-D-glucose units, also called *N*-acetylglucosamine, able to form hydrophilic bonds and relative strong structures when proper additives are employed. Thereafter, as a secondary innovative aspect, the design-of-experiment (DoE) technique has been employed to develop numerically the coating formulation, ensuring the necessary control when biological and/or leftovers materials are employed. This statistical methodology can be used to overcome the strong limitations intrinsic to the one-factor-at-a-time (OFAT) method, reducing the number of experiments needed to provide the maximum information content and therefore saving both time and resources.[22] In fact, statistically reliable models describing the correlation between coating formulation and selected output variables, responses that are to be examined downstream the experiment, can be generated through analysis of variance (ANOVA).

The secondary aim of this study is to develop complete sustainable CRFs containing all of the three essential elements for the growth of a plant (nitrogen, phosphorus, and potassium (NPK)). Thereafter, in a strong circular economy perspective, two types of lightweight aggregates (LWAs), previously developed for this scope and based on leftovers and

byproducts, have been investigated as a core for the coating.[23−25] Coated LWAs have been characterized to evaluate the coating strength, density, pH, and electrical conductivity. Controlled-release tests in citric acid have been performed on all coated LWAs, until 21 days, to evaluate the release of nutrients and toxic substances. Citric acid has been employed instead of water to follow the European Standard EC Regulation No. 2003/2003[26] that must be applied in our geographic region, thereafter promoting the perspective of this study.

■ RESULTS AND DISCUSSION

Raw Material Characterization. Chemical and elemental analyses (Table 1) performed on core and shell materials

Table 1. Chemical (X-ray Fluorescence (XRF)) and Elemental (Inductively Coupled Plasma (ICP)) Analyses of the LWAs and BSF Biomass in wt %[a]

	oxide (wt %)	C-Glass	C-Ash	BSF biomass
macronutrients	K_2O	3.88	8.40	1.09
	P_2O_5	4.47	5.63	1.98
secondary	SiO_2	52.69	47.35	<0.05
	CaO	7.29	8.85	1.52
	MgO	1.78	2.77	0.89
	Na_2O	1.57	0.75	1.10
micronutrients	Fe_2O_3	4.50	5.70	<0.05
others	Al_2O_3, TiO_2	21.61	19.81	<0.05
toxic	PbO	<0.05	<0.05	<0.05
	L.O.I.	2.18	0.70	93.34
element	N	0.13	0.08	7.90
	C	0.01	0.02	46.23
	H	0.01	0.01	7.44
	S	0.04	0.25	0.00

[a]XRF sensibility, ±0.05; ICP sensibility, ±0.01.

separately confirm the high organic content of BSF biomass due to the significant loss of ignition (L.O.I.), above 90 wt %, and remarkable carbon content. As shown in Table 1, BSF biomass makes an excellent source of nitrogen (near to 8 wt %) to be released in soil, while limited contents of phosphorus and potassium oxides can be detected, 1.98 and 1.09 wt % respectively, in the chemical analysis reported. With regard to uncoated LWAs, the chemical analysis indicates high percentages of silicon and aluminum oxides due to the presence of red clay, as well as for iron and magnesium oxides. The relevant presence of phosphorus and potassium oxides is confirmed in both the LWAs. Both aggregates show very low values of loss of ignition (L.O.I.), and this is consistent with firing treatment at around 1000 °C needed to obtain these aggregates.[23] As suggested from the elemental analysis of C-Glass and C-Ash, no significant concentrations of other elements are detected, confirming again the predominance of inorganic matter. No significant content of toxic compounds, such as heavy metals or chlorides, has been detected both in LWAs and BSF biomass, suggesting that the employment of these materials should not deliver toxic substances to the soil.

Due to its high organic content, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) have been performed on BSF biomass to investigate carefully the degradation profile and related coating manufacturing preparation and application onto the core. As shown in Figure 1, the BSF biomass degradation curve indicates a fairly stable
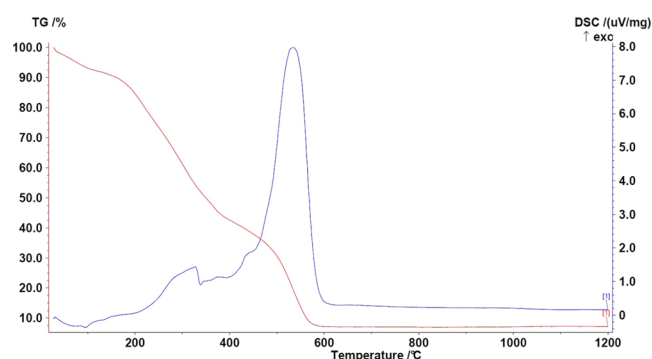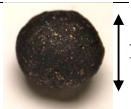
Figure 1. DSC and TG analyses of BSF biomass.

Table 2. Preliminary Formulation with Different Plasticizing Agents in wt %[a]

	BSF (wt%)	Water (wt%)	GL (wt%)	PEG400 (wt%)	CMC (wt%)	Result
P1	46.15	7.69	46.15	/	/	1.5 cm
P2	60.00	10.00	30.00	/	/	
P3	66.67	11.11	/	22.22	/	
P4	54.55	9.09	/	36.36	/	
P5	66.67	22.22	/	/	11.11	
P6	70.59	23.53	/	/	5.88	

[a]The indicated scale bar should be applied for all of the pictures in this table.
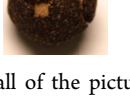
situation before 200 °C, with a limited decrease in the weight of the sample in proximity to a small endothermic peak, which implies the sole loss of moisture inherent to the material. In the range from 250 to 600 °C, several exothermic peaks can be detected on the DSC curve, with particular relevance at around 300 and 550 °C due to the combustion of the organic fraction. These peaks are in fact accompanied by an overall considerable weight loss, detected through TG, near to 50 wt % for the former and near to 80 wt % for the latter. Above 600 °C, no further peaks are detected; therefore, no more significant thermal decomposition occurs. At the end of the TG curve, only a small fraction of the BSF biomass appeared that was not degraded above 600 °C due to the presence of mineral compounds, which can be attributed to the chitin fraction of the insect. This result is consistent with the chemical analysis shown in Table 1, wherein negligible amounts of K_2O, P_2O_5, CaO, and Na_2O have been assessed for the BSF biomass. Considering these results, it is clear that BSF biomass cannot be added to the LWA formulation directly because it will decompose during firing at 1000 °C, and for coating processing, only temperatures below 600 °C must be considered to avoid further energy consumption.

Preliminary Tests with Different Plasticizing Agents. Preliminary tests have been carried out to identify the most promising plasticizing agent to be added to the BSF biomass; in fact, water alone is not enough for the formation of a durable coating due to too fragile behavior of the BSF biomass itself. In fact, it must be considered that, for a reliable measurement of the complete fertilizer's nutrient release, a homogeneous and well-adherent coating is necessary. As shown in Table 2, PEG400 and critical micelle concentration (CMC), used separately, led to the formation of coatings with poor cohesion and adhesion due to the significant presence of defects, e.g., holes in the coating layer. This effect is probably due to phase separation of the coating into BSF biomass-rich and plasticizer-rich regions.[27] In fact, PEG400, consisting of short aliphatic chains capped with hydroxyl groups, is able to constitute fewer hydrogen bonds with polypeptide chains, such as proteins, with respect to glycerol for example. On the other hand, CMC as a polysaccharide interacts with N-enriched groups, altering their rigid structure and causing a reduction of hydrogen bonds among macromolecule chains.[28] Glycerol employment leads to the most durable coating formation and best adhesion to LWAs, as seen from Table 2. In fact, glycerol, reacting with a N-enriched fraction of BSF biomass due to its low molecular weight that promotes the diffusion into macromolecular chains, reduces internal hydrogen bonding within the BSF biomass molecules owing to its highly

hydrophilic characteristics, leading to a more compact layer.[29] In addition, it must be also considered that the role of the polar group (−OH) is relevant to the polymer–plasticizer interaction. In fact, increasing the polar groups makes this interaction stronger.[30] In our case, glycerol, among three highly hydrophilic plasticizers, is the most suitable in terms of low molecular weight, better penetration into the proteins, and the amount of the polar group. Water addition is necessary for all formulations to both decrease the percentage of the plasticizing agent and improve the plasticity of the mixture, thereafter making easier the covering of the LWAs. The use of C-Glass or C-Ash aggregates does not lead to significant differences in coating formation. Figure 2 presents detailed micrographs of coating P1, obtained with glycerol, on C-Ash LWAs to underline the absence of specific microstructural patterns (Figure 2a), leading to a homogeneous structure of the layer, and to evaluate the thickness of the coating, being around 0.7 mm (Figure 2b).

Coating Formulation through Mixture Design. Glycerol has been chosen as a plasticizer for coating formulation, and the ranges for the Mixture Design employed are defined in Table 3, as a result of the preliminary tests, as well for water and BSF biomass. Moreover, the type of coated LWA (C-Ash or C-Glass) has been considered.

Taking into account the 26 experiments detailed in Table 4, LWA-coated aggregates have been realized and characterized. For the first panel, the test has been employed to rate coating adhesion, which is the most important property to obtain a coated LWA; thereafter, coating cohesion and manufacturing efficiency have been taken into account to estimate coating quality; and finally, apparent density has been measured. All of the results have been reported in Table 4, as well as their errors, resulting in statistical reliability when compared to the
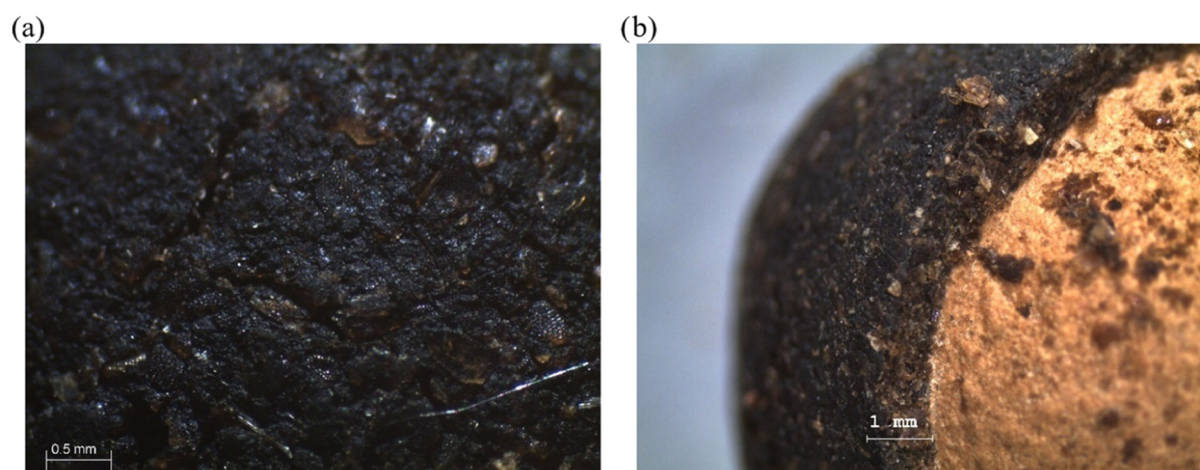
Figure 2. Optical micrographs of coated C-ASH with P1 coating composition at different magnitudes and positions: (a) 25×—surface and (b) 12.5×—cross section.

Table 3. Mixture Components and Their Ranges in Terms of Real Values (wt %)

component	name	units	type	minimum	maximum
A	water	%	mixture	0.000	35.000
B	glycerol	%	mixture	0.000	42.851
C	BSF	%	mixture	50.000	90.000

factor	name	units	type	minimum	maximum
D	PK		categoric	C-Glass	C-Ash

related average value. From a rough evaluation of the data, BSF biomass must be limited to the range 50−56% to ensure good coating adhesion, whereas for the other mixture components, it is not possible to determine any trend without the multivariate analysis. Also, for the other two responses, coating cohesion and manufacturing efficiency, no trend is immediately achievable without an in-depth analysis. As seen from Table 4, all of the apparent densities measured are included in the range 1.2695−1.4667 g/cm^3, therefore showing a restrained value of the density suitable to define an LWA formulation.

The ANOVA results are presented in Table 5, showing that all of the responses generate models with significant correlation among data as confirmed by the p-value < 0.0001, meaning that the probability of data variation due to unknown factors is statistically irrelevant. Moreover, Table 5 shows that the lack of

Table 4. Complete Experimental Plan

run	water (%)	glycerol (%)	BSF (%)	D/PK	coating adhesion	coating cohesion	manufacturing efficiency	apparent density (g/cm^3)
1	10.00	0.00	90.00	C-Glass	0	0	0	
2	10.00	0.00	90.00	C-Ash	0	0	0	
3	34.82	0.00	65.18	C-Glass	0	1	0	
4	34.82	0.00	65.18	C-Ash	0	1	0	
5	35.00	0.00	65.00	C-Glass	0	1	0	
6	35.00	0.00	65.00	C-Ash	0	1	0	
7	0.00	10.00	90.00	C-Glass	0	1	0	
8	0.00	10.00	90.00	C-Ash	0	1	0	
9	0.00	25.00	75.00	C-Glass	0	2	0	
10	0.00	25.00	75.00	C-Ash	0	2	0	
11	17.50	12.50	70.00	C-Glass	0	2	0	
12	17.50	12.50	70.00	C-Ash	0	2	0	
13	13.89	25.00	61.11	C-Glass	0	2	0	
14	13.89	25.00	61.11	C-Ash	1	2	1	
15	19.00	25.00	56.00	C-Glass	1	3	1	1.4327 ± 0.0219
16	19.00	25.00	56.00	C-Ash	1	3	1	1.2661 ± 0.0425
17	35.00	11.76	53.24	C-Glass	1	4	2	1.3797 ± 0.0683
18	35.00	11.76	53.24	C-Ash	1	4	1	1.1948 ± 0.0163
19	35.00	15.00	50.00	C-Glass	1	6	2	1.3448 ± 0.0279
20	35.00	15.00	50.00	C-Ash	1	6	2	1.2390 ± 0.0352
21	25.00	25.00	50.00	C-Glass	1	5	3	1.3991±0.0405
22	25.00	25.00	50.00	C-Ash	1	5	3	1.2695 ± 0.0095
23	7.15	42.85	50.00	C-Glass	1	6	3	1.4667 ± 0.0827
24	7.15	42.85	50.00	C-Ash	1	6	3	1.3787 ± 0.0054
25	10.00	30.00	60.00	C-Glass	1	4	3	1.3469 ± 0.0193
26	10.00	30.00	60.00	C-Ash	1	4	2	1.3229 ± 0.0413

Table 5. ANOVA Results

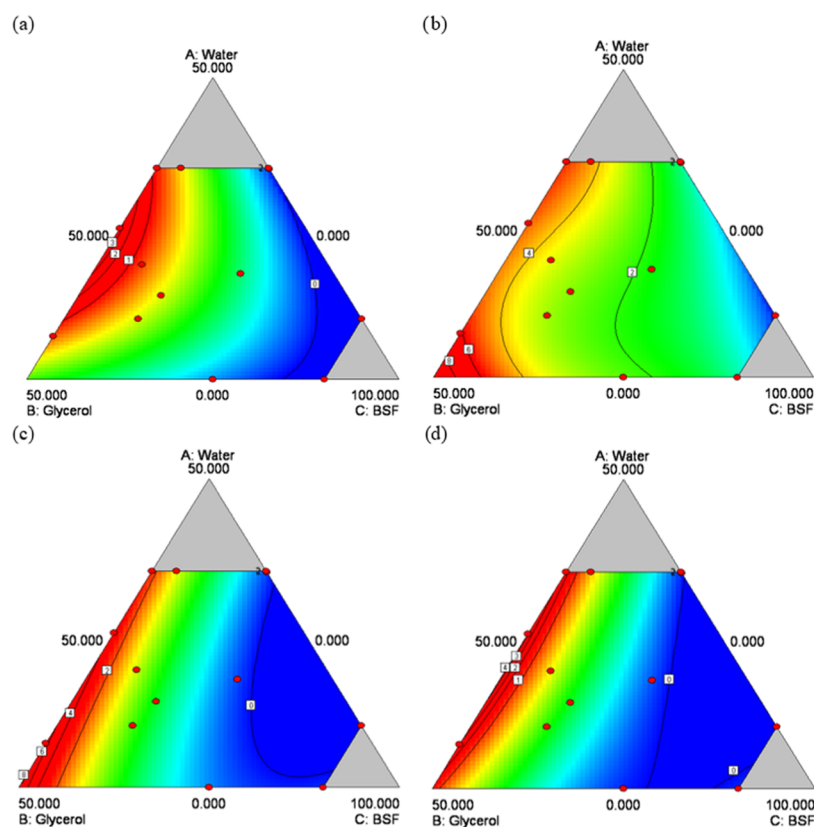| responses	transformation for normalization	p-value	lack of fit	significance terms	R^2	Pred–R^2
coating adhesion	ln	<0.0001	not significant	A, B, C, AB	0.78	0.74
coating cohesion	square root	<0.0001	not significant	A, B, C, AB	0.96	0.94
manufacturing efficiency	ln	<0.0001	not significant	A,B,C, AC, BC	0.84	0.78
apparent density	ln	<0.0001	not significant	A,B,C, AC, BC	0.80	0.75

Figure 3. Contour plots of the models: (a) coating adhesion, (b) coating cohesion, (c) manufacturing efficiency, and (d) apparent density (g/cm^3).
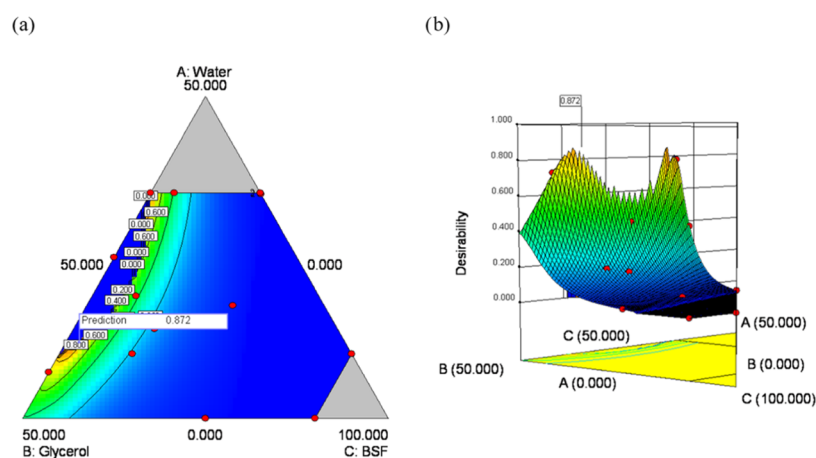
Figure 4. Graphical result of the desirability function: (a) 2D and (b) 3D.

fit is not significant, allowing us to conclude that models are significant. A logarithmic transformation has been required to normalize the data and codify the hierarchy of the factors for all of the responses, except for coating cohesion that has needed a square root transformation. In addition, it is worth noting from Table 5 that, analyzing the significant factors, the only one that is not significant for all of the investigated

responses is the type of the LWA core (C-Ash/C-Glass), indicating that the difference among vitrified and not vitrified cored does not affect the selected responses. R^2 and Pred-R^2 (Table 5) confirm the good fit of data and the more than acceptable predictive power of the model, with values quite close to 1.00, confirming that the models can be employed in a predictive perspective. A normal distribution of the residuals

has been analyzed (data not reported), confirming that each model can be used to explore the region of interest.

The contour plots (Figure 3) better explain the responses related to coating properties as a function of the amount of each mixture component, indicating that single factors but also their interactions contribute to explain the correlation between compositions and selected responses. In particular, a very similar trend is shown for all of the response: The quantity of N-enriched BSF must be very near to 50 wt % to maximize all of the response (red areas), therefore, a non-negligible quantity of the water−glycerol mixture is needed to obtain suitable coating for this application. In particular, coating adhesion (Figure 3a) results are promoted by a mixture containing around 50 wt % N-enriched BSF, 25 wt % water, and 25 wt % glycerol, whereas coating cohesion (Figure 3b) is promoted by a higher content of glycerol, keeping fixed the same quantity of BSF biomass. On the other hand, the manufacturing efficiency (Figure 3c) and apparent density (Figure 3d) seem to be not particularly affected by changing the water/glycerol proportion, keeping always fixed BSF biomass near to 50 wt %. A rational approach such as mixture design allowed us to point out how small changes in composition can yield considerable results in practice, occurring when interaction among a non-negligible number of components takes place. In this case, we have demonstrated that the amount of N-enriched BSF into the coating formulation is the most important factor, whereas only a limited but non-negligible effect is due to the proportion among glycerol and water.

Figure 4 shows the two-dimensional (2D) and three-dimensional (3D) plots of the overall desirability function over the investigated ranges. According to the results obtained for each model, the set of conditions with the highest desirability value is considered as the optimum combination for the required responses. The target and priority (importance) of every single property are classified in Table 6 to derive the overall desirability function D as defined in the

Table 6. Desirability Function Conditions

responses	goal	importance
coating adhesion	=1	5
coating cohesion	to maximize	5
manufacturing efficiency	to maximize	2
apparent density	to maximize	4

Methods section. The data reported in that table have been established based on the specific behavior needed for the tailored application of these coatings: the highest importance has been attributed to the adhesion between the coating and the core. Lower importance has been allocated to manufacturing efficiency and coating cohesion because, nevertheless their importance, these aspects are mainly related to well-delimited breakages of the coating, not effecting its overall function. As well as for apparent density that could poorly affect only the nutrient release efficiency without precluding coating formation.

As shown in Figure 4, the overall desirability shows high changes, moving from the formulation with the N-enriched BSF content from 50 to 60 wt %, indicating that small variations around the best condition (yellow area) will significantly change the overall desirability. The highest desirability, with values very close to 0.87 (1 is the maximum), is obtained by employing about 50% of N-enriched BSF,

whereas the other two components may vary from 9 to 32 wt % (water) and 17 to 40 wt % (glycerol). In particular, the composition containing 12 wt % water, 36 wt % glycerol, and 52 wt % BSF biomass has been reproduced on several samples and employed for validation of the analysis, showing good performance in terms of adhesion and cohesion and therefore the good predictive power of the analysis.

Coated LWA Characterization. The apparent density values (Table 7) show that no significant variation of the

Table 7. Physical and Agronomic Properties

	C-ASH	C-Ash coated	C-Glass	C-Glass coated
pH	6.52	6.47	7.31	6.46
conductivity (dS/m)	0.97	7.71	0.22	8.38
apparent density (g/cm^3)	1.27	1.29	1.49	1.43
germination index (%)	136	80	147	75
growth index (%)	119	228	77	178

coated LWAs can be detected with respect to uncoated aggregates and that the density of the aggregates formed by the glass is higher with respect to the others where ashes are included. This result agrees with the apparent densities of the coatings, as shown in Table 4, and confirms that even after the coating process lightweight aggregates can be obtained. The pH and conductivity measurements (Table 7) have shown instead a significant variation due to the coating process. Indeed, the pH of uncoated C-Glass decreases strongly by the coating, reaching values near to an overall neutral condition, more suitable for compounds that should act as fertilizers, avoiding high pH variations of the soil. Concerning conductivity, a high increase can be observed after the coating application, suggesting significant ion mobility, for both the LWAs, far to respect the limit generally applied to fertilizer compounds (<2 mS/cm). This result is surely due to the coating material itself and its low resistance after immersion in water, a condition in which the conductivity is measured; therefore, this negative result can be probably related to the measurement procedure that is not reflected by the real employment conditions.

Release Tests of LWA Nutrients. Release tests performed in dynamic conditions lead to a fast (30 min) disintegration of the coating; therefore, static test results have been considered as a procedure that better reflects the conditions of fertilizer's release during real applications. Phosphorus release tests (Figure 5a) of the uncoated LWAs show only partially controlled release occurring after almost the first 7 days (near to 40% of the overall final 50%) for both types of LWAs. Significant differences among C-Ash and C-Glass samples resulted as the employment of ashes directly into the LWA composition led not only to an increased uncontrolled nutrient release effect but also to a greater final release compared with the employment of fertilizer glass (60 vs 40%). Due to data normalization over the LWA composition, this result can be explained considering the ability of the fertilizer glass to retain the macronutrients, avoiding their release. The release control over time is strongly improved by the coating application, in which a gradual increase of release is observed moving from 30 min to 21 days for both LWA types, even though a decrease of the final release is observed (near to 45 wt %) with respect to C-Ash. A similar trend can be observed for potassium (Figure 5b) even when the overall release is lower than that of
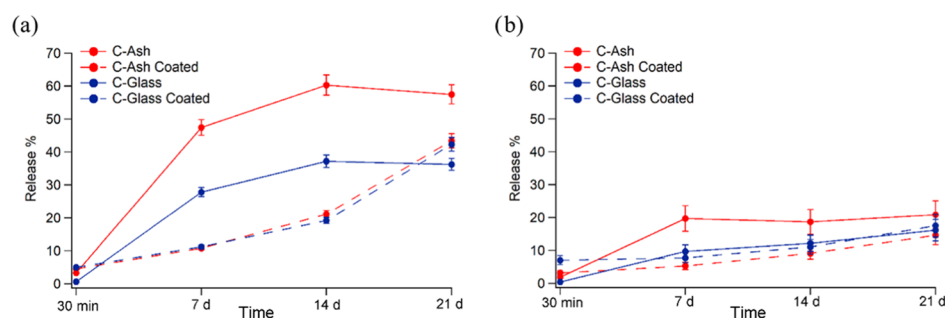
Figure 5. Release test: (a) phosphorous and (b) potassium.

phosphorus, near to 70% and 50%, respectively, for uncoated and coated LWAs. These results are consistent with the fact that the coating can act as a physical barrier for a longer time and thereafter control the release of the other nutrients. These results show that core−shell systems studied in this research are potential candidates as slow-release fertilizers, also considering that the data trend of the release is not oriented to exceed 75% in 28 days, as confirmed by the previous test focused on the core.[7,31] Moreover, a more controlled release can be obtained with respect to other systems detailed in the literature on biodegradable polymers from agroresidues/clay, suggesting a complete release within 24 h.[32] For nitrogen release, preliminary results suggest a strong release of this nutrient (near to 50% therefore equal to 70.85 mg of nitrogen for each sample, considering the results shown in Table 1, and an average amount of 1.79 g of BSF biomass for 10 g of sample in total) but in a too short time to be considered as controlled release (7 days), probably due to too fast diffusion of nitrogen through the coating. Therefore, more effort should be done to optimize the coating formulation to increase the controlled release of nitrogen over time.

LWA Germination and Growth Tests. To investigate the possible phytotoxic effect of this core−shell slow-release fertilizer, germination and growth tests in vivo have been realized, and the data are reported in Table 7. These results confirm the positive effect of the fertilizer for plant growth, increasing drastically the measured growth index with respect to uncoated LWAs (near to +100%). On the other side, the restrained germination index has been measured after the coating process (near to −45%), indicating that better performances of this core−shell fertilizer are detectable during a quite long period of application, increasing its potential as a slow-release fertilizer. Coated LWAs, obtained through a well-tailored mixture of glycerol, water, and BSF biomass, were subjected to physical, release, and agronomic tests, confirming that they positively act as slow-release fertilizers over 21 days of use. In fact, a barrier action of the coating can regulate the release of potassium and phosphorous. Further investigations should be performed into the coating's mechanical resistance for industrial dispersion in soil.

CONCLUSIONS

In this work, ceramic LWAs, containing phosphorus and potassium, were covered with a N-enriched coating, generated from insects rearing on wastes (poultry dejections), demonstrating a strong circular economy perspective. Moreover, the coating was designed and implemented on the LWAs by the design-of-experiment method, which allowed us to increase the laboratory test efficiency, reducing their number but exploiting

as much information as possible and calculating mathematical models for formulation development. First, a complete characterization of the N-enriched BSF biomass was performed, confirming that no dangerous substances are contained in it and an overall content of nitrogen of 7 wt % was detected. The thermal analysis suggested that only low-temperature treatments were able to avoid the degradation of this organic fraction, minimizing also the energy needed; therefore, a mixture design was employed to formulate a paste to be used as a coating for the LWAs based on this organic compound. Coated LWAs, obtained through a well-tailored mixture of glycerol (better behavior with respect to other plasticizer agents tested), water, and BSF biomass, were subjected to physical and release tests, confirming that they respond positively to the main requirements needed for slow-release fertilizer employment over 21 days of use. In fact, a barrier action of the coating has also been obtained, regulating the release of other nutrients. The good behavior of glycerol is an important point because high amounts of this substance are produced as a byproduct of biodiesel production; therefore, easy availability and low price can be obtained. In addition, slow release during time is enhanced with the addition of ashes directly into the lightweight composition with respect to samples containing fertilizer glass due to the barrier effect of the glass. As future perspectives, a more controlled release could be obtained by testing new coating formulations and manufacturing processes to improve the compactness of the coating itself for an industrial scale-up perspective.

METHODS

Raw Materials from Residues. LWAs employed as a base for the coating were obtained from agrifood industrial or postconsumer activities geographically near to each other with the aim to promote the re-employment of local wastes (north Italy). LWAs' base was a local red clay (from a quarry in the province of Modena), in which 15 wt % spent coffee grounds were included as a poring agent, taking advantage of their combustion during sintering of the ceramic matrix following the results of a previous study.[23] Potassium and phosphorous were introduced into LWAs using vegetable biomass and bone flour ash as they were or through a well-tailored glass, named fertilizer glass. This glass is based on an industrial secondary raw material, named glassy sand, coming from the secondary treatment of packaging glass cullet (90 wt %) and an old cathode-ray tube screen glass recycling process (10 wt %) produced by an industry in the Piemonte region (still in northern Italy). Two LWA compositions named C-Ash, containing 24 wt % PK-enriched ashes, and C-Glass, containing the same quantity of PK-enriched fertilizer glass,

were chosen as the core for the coating tests. The BSF biomass was derived from prepupae reared on a substrate consisting of poultry dejection and characterized by the following composition (dry matter): 33 wt % proteins, 38 wt % lipids, 19 wt % minerals, and 10 wt % chitin.[20] The N-enriched fraction of BSF biomass was employed in the present study and obtained through a chemical extraction process that aimed to separate the lipid fraction from the N-enriched fraction.[19,20] All of the chemical and elemental compositions of the raw materials are reported in Table 1. Glycerol (GL, Sigma-Aldrich, 99%), carboxymethylcellulose (CMC, $M_w \sim 700$, Sigma-Aldrich), and polyethylene glycol (PEG400, Honeywell Fluka, MM = 400) were tested as plasticizers.

Preparation of LWAs. To obtain LWAs, clay was manually mixed with the residues until complete homogenization and then distilled water was added to obtain a workable paste. Subsequently, LWAs with spherical shape were realized manually by employing 2 g of mixture for each one. Subsequently, all of the prepared LWAs were dried at the same time in an oven at 105 ± 5 °C to remove free water and to prevent the possible cracking of the aggregates during firing due to sudden evaporation. Finally, LWAs were fired at 1000 °C for 60 min in a hot oven, obtaining the sintering of the ceramic and glass components and the combustion of the organic fraction. After sintering, LWAs were extracted from the oven and allowed to cool to room temperature.

The N-enriched BSF biomass was dried in the oven at 65 ± 5 °C to remove free water and then ground using a laboratory mill (IKA A10 B) and sieved to obtain a powder with $D_{50} < 250$ μm to get a homogeneous powder to be mixed. Manual mixing of this fraction of N-enriched BSF biomass, plasticizer, and water was employed to obtain homogeneous pastes following the formulations in Table 2. Thereafter, 0.75 g of each one of these pastes was applied on LWA surfaces, previously dried in the oven at 120 °C for 24 h, until a homogeneous layer was formed with good adhesion to the substrate core. Coated LWAs were then dried at room temperature under a fume hood for 48 h before characterizations.

Coating Design through a Mixture Design Approach. The coating formulation was designed by the mixture design approach, which is a well-tailored DoE tool for mixture composition investigation. In mixture design, two main constrains were used: the first regarding the relative proportion of the constituents in the mixture and the second taking into account the additional boundary constraints related to all mixtures. Moreover, also the core type (PK) was taken into account as a factorial variable; therefore, a combined-mixture design was employed to set up the experimental plan and analyze the measured data. The Design Expert 8.0 (Stat-Ease) code was used; therefore, to manage this specific experimental region, the Computer Aided D-optimal Design was used. Three factors were considered as coating mixture components: water, glycerol, and N-enriched fraction of BSF, which were varied according to the ranges detailed in Table 3 and from which the experimental plan of Table 4 was derived.

Mixture model forms (MMFs), most commonly used in fitting data, are the canonical polynomials known as the Scheffe canonical given by

$$\text{MMF} = \sum_{i=1}^{q} \beta_i \times x_i + \sum_{i<j}^{q} x_i \times x_j \times \beta_{ij} \tag{1}$$

where β_i and β_{ij} are the regression coefficients calculated from the experimental data by multiple regression and x_i and x_j are the levels of the independent variables. The number of experiments required for this experimental plan was equal to 26, and in addition, five replicates for each experiment were performed for error estimation. Finally, mixture preparation and application onto the core were performed according to the randomized run order to avoid environmental conditioning.

Analysis of variance (ANOVA) was employed to evaluate the model significance and its predictive power to describe the relationships between mixture components and selected properties. In particular, the statistical difference among samples can be defined when the variation among all of the samples, usually due to process or factor changes, is larger enough than the variation within the samples obtained in the same experimental conditions. Regression coefficients were analyzed by the p-value approach: p-values higher than 0.005 were not considered statistically significant and therefore neglected for the model formulation.[22] The quality of fit in terms of regression analysis and the prediction power of the models were evaluated by R^2 and Pred-R^2. R^2 is the proportion of the variance of the response, which is estimated from the independent factors, and Pred-R^2 is similar to R^2 but calculated through the predicted values of the response. Response contour plots were used as functional tools in explaining graphically the role of the main components on the final considered properties. In this type of plots, the red area suggests conditions under which the explored property reaches its higher values, whereas the blue area indicates the region with lower values of the same property. Intermediate colors from red to blue suggest a progressive transition from higher to lower values and vice versa. The red dots, eventually present, normally detect points measured during the study in the experimental region. Finally, the overall desirability function (D) was employed to calculate the most desirable response values, taking into consideration all of the analyzed responses at once, weighed for their importance on the final goal.

Characterizations. The evaluation of the capability to constitute a suitable coating was performed through a consensual panel test, and the scores obtained were recorded as responses and then analyzed by statistical methods. The panel test was carried out by employing the judgments of five people who were not informed about the conditions of the experiment. The output of each experiment was evaluated considering the homogeneity of the coating after drying (coating cohesion) and therefore its ability to stick the LWAs (coating adhesion). Moreover, the workability of the mixture in terms of the loss of material during the coating process was considered (manufacturing efficiency). For all of the responses, the classification number equal to the lower value corresponds to the weakest quality and the highest score corresponds to samples with the highest quality (e.g., coating completely homogenous and adherent to the LWAs on all of the surface with good paste workability and restrained the loss of material).

Elemental and chemical compositions of LWAs and BSF biomass were measured through X-ray fluorescence (XRF, ADVANT'XP+, Thermo ARL) and inductively coupled plasma atomic emission spectrometry (ICP-AES), respectively. Differential scanning calorimetry (DSC, Netzsch, DSC 404), performed in air at a heating rate of 10 °C/min using 30 mg of powdered sample, and thermogravimetric analysis (TGA, Netzsch, DSC 404), performed on 15 ± 2 mg of powdered

sample using a temperature ramp of 10 °C/min from 0 to 1200 °C in an inert atmosphere (nitrogen, 50 mL/min), were used for the determination of the degradation profile of raw materials. The analysis of the particle size distribution of the BSF biomass was performed by the laser diffraction method in water (Mastersizer 2000 particle size analyzer with a Hydro-S wet dispersion unit, Malvern Instruments Ltd., Malvern, U.K.).

Micrographs of the coated samples were taken through an optical microscope (Leica Microsystems, DM500). The apparent density was calculated as the ratio between the average weight and volume measured over 10 samples. The weight was measured through an analytical balance (Bel Engineering M124A) with a full scale of 120 g and an accuracy of 0.0001 g, and volume, assuming a spherical shape of the LWAs and measuring the diameter through digital a micrometer (Mitutoyo, YY-T1BD-2GYE; sensibility, 0.02 mm). Chemical tests such as pH (pH meter, XS Instruments, pH 6), according to European standard EN 13037:2012, and conductivity (Oakton portable conductivity meter model CON 6/TDS 6) measurements following the ECE parameter (electrical conductivity on the saturated extract) were performed on all LWAs.

Release tests in 2 wt % citric acid solution were performed to evaluate the release of nutrients such as potassium, phosphorus, and nitrogen at 30 min and 7, 14, and 21 days, following the European legislation about the test on phosphorus release (Method 3.1.3) in static conditions.[26] A sample of 10 g of fertilizer was immersed in 1000 mL of solution, and after each different time of release, 95 mL of solution was picked up and filtered with a 0.45 μm filter for the analysis. Thereafter, the measured concentration was proportioned to the real amount of solution at the time of solution collection. The analysis of the solution was performed by the plasma emission spectrometry technique (Agilent Model 7500a ICP-mass spectrometer; sensibility, 0.01%) and normalized to the effective quantity of the solution employed for the analysis.

Finally, germination and growth tests were performed following the standard UNI 10780:1998 Appendix K and Appendix L, respectively.[33] Both germination and growth indexes express the percentage performance ratio between the investigated fertilizer and a standard control; an index equal to 100% means the same performance, while percentages higher or lower indicate respectively better or worse performance than the standard sample. Basil seeds were employed (five seeds for each test) under an LED light (45 W). The germination was evaluated by monitoring the number of shoots, while the growth was measured in terms of plants' height after 40 days. Plants' height was measured through a digital micrometer (Mitutoyo, YY-T1BD-2GYE; sensibility, 0.02 mm) on an average of 10 measurements.

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Notes

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