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Biodegradable soy protein-based tablets for the controlled release of zinc

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ABSTRACT

Controlled-release systems are gaining interest in the horticultural industry to supply fertilizers to crops. However, their manufacturing process increases their cost, making its industrialization difficult. In this context, compaction of powders could be a low-cost and easily industrializable alternative. Thus, the main objective of this work was the manufacture of soy protein-based tablets with zinc (micronutrient) incorporated using different compaction parameters (pressure: 333, 416 and 777 MPa; post-manufacture heat treatment: 4 and 24 h). Thus, the mechanical (dynamic compression tests) and microstructural properties (SEM and grain number) of the different tablets were evaluated to study the effect of pressure and temperature on them. In addition, water uptake capacity and micronutrient release were studied. The latter has been analyzed with the use of two theoretical models (Higuchi and Korsmeyer-Peppas) to evaluate which model is the most accurate for predicting the zinc release of the different tablets. The results presented in this work demonstrate the great utility of soy protein-based tablets for the controlled release of zinc. Thus, this process allows the incorporation of 116 g of Zn in a kg product that can be released under control (9–10 h in water). These products have great industrial potential due to their ease of processing and properties, making them economically competitive.

1. Introduction

The current fertilization method is not very effective, as most fertilizers drain into the subsoil or groundwater due to the low assimilation of them by crops, thereby contaminating them with nutrient excess (Kondraju and Rajan, 2019). For this reason, it is necessary to look for new alternatives to regenerate farmland nutrients. Thus, different techniques, such as conservation tillage and crop rotation, have been tested. These techniques consist in dividing the farmland, cultivating one part of it while the other is regenerated by crops without nutrient needs (tillage) or by not planting any crops (rotation). However, these techniques deteriorate the harvested croplands, making it less versatile and slower and causing the production yield to drop, whereas other techniques, such as fertilization, can regenerate the farmland without such loss (Cárceles Rodríguez et al., 2022).

Therefore, new research lines on the advantages of fertilization should be studied. A new field of increasing interest is the use of slow- or controlled-release fertilizers (Yang et al., 2020). These systems could be adapted to the needs of crops, improving assimilation efficiency by plants (Tibães Kamimura et al., 2020). Bioplastic matrices are attracting attention in this application. These materials can support the fertilizers and release them in a controlled way through the irrigation of water or the biodegradation of the bioplastic matrix, improving fertilizer efficiency. In this context, several authors have evaluated different proportions of nutrients or processing methodologies with the aim of optimizing the elaboration of these materials. For example, Souza et al. (2018) processed a starch-polyhydroxybutirate matrix for the release of sodium and potassium by mixing and compression molding. In the same line, Lu et al. (2022) reflected all the benefits of lignin matrices for the slow release of nutrients such as urea. On the other hand, Mesias et al. (2019) and Kartini et al. (2020) investigated more sophisticated methods, such as hydrogel formation by chitosan and solvent casting with carboxymethyl cellulose, respectively, in order to control the release of NPK (nitrogen, phosphorus and potassium). All these studies show that the study of the influence of the kinetics of nutrient release with the parameters of the process used, as well as the raw materials, could facilitate the adjustment of the release to the needs of each crop, which requires their modulation. Thus, more specialized fertilization

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can be obtained, improving its production yield and reducing its cost and pollution.

This kinetic modulation can be realized by different empirical mathematical models (Oh et al., 2011). Higuchi was one of the precursors. He established a model based on Fick's law. The model proposes that a principle dissolved or embedded in a solid polymer tends to diffuse towards its surface (Dredán et al., 1996). This mechanical model is the simplest, as it only contemplates one release phenomenon, being usually used. However, this approximation is not always true (Siepmann and Peppas, 2011), which led Korsmeyer and Peppas to propose a more general equation, where other release mechanisms are contemplated in order to improve the kinetic modeling (Korsmeyer et al., 1983):. In this way, physical properties, such as molecular weight and solubility, matrix geometry, the amount of drug incorporated, matrix surface area and matrix density are considered (Boncel et al., 2013).

Biodegradable controlled-release systems are processed by non-conventional industrial methods, such as the fabrication of hydrogels or lyophilization (Mesias et al., 2019; Shen et al., 2020), which are difficult to industrialize. In addition, there are other processing methodologies that imply a large number of steps, requiring a long time to obtain the product and thus increasing its cost (Jiménez-Rosado et al., 2020d; Ni et al., 2010). In this sense, the use of processes already industrially implemented with faster production can improve their commercialization. In this context, compaction of protein powders by compression can be an interesting alternative. This technique consists of applying pressure to a mixture of powders. In this way, the grains that make up the powder are plastically deformed, creating a surface tension that holds them together in the shape of a tablet (Vass et al., 2020). Additionally, a heat treatment of the pieces after compaction can be used to strengthen the mechanical properties of the tablet, as in other compaction systems (Zavadiuk et al., 2020). This is a simple, low-cost and easily industrializable process. Thus, controlled-release tablets can be obtained at a low price, which allows them to compete with conventional fertilizers in the current market. This competitiveness is given due to the benefits that these systems can generate in contrast to conventional fertilizers since they involve less loss of fertilizers due to leaching (greater assimilation of the same by the plants), in addition to an extra stimulation of the protein that makes up the matrix (Jiménez-Rosado et al., 2023a). Although these benefits were also generated by the exposed controlled-release systems, their processing method did not make them economically feasible on an industrial scale, while the method proposed in this study, due to its simplicity, would allow easy scaling.

In this context, the novelty of this work is the use of a more straightforward and more industrializable technique, i.e., compaction of powders, for the elaboration of controlled-release systems, making them more competitive with conventional fertilizers. Thus, the main objective of this study was to develop soy protein-based tablets with zinc incorporated for their controlled release in crops, using compression molding as processing method. Soy protein was chosen due to its low cost as a by-product in the production of soybean oil, which can further reduce the price of the final product (Capezza et al., 2019). On the other hand, zinc was selected as a micronutrient to be incorporated due to its great influence on the crop. Thus, low amounts of zinc could cause yield losses of up to 60%, while an excess of it can cause crop intoxication (Suganya et al., 2020). Since the compaction pressure and the subsequent heat treatment can influence the functionality of these tablets, different pressures (333, 416 and 776 MPa) and heat exposure times (0, 4 and 24 h) were studied. Thus, the mechanical and morphological properties, as well as the controlled release capacity and water uptake capacity, were evaluated for each selected parameter, modulating their behavior.

2. Materials & methods

2.1. Materials

Soy protein isolate (SPI) was used as the matrix of the tablets. This protein is a by-product of the industrial production of soybean oil. Its composition is mainly protein (91 wt%), with some humidity (max. 5 wt %) and other minority components (max. 5 wt%). SPI was supplied by Protein Technologies International (SUPRO 500E, Belgium) in the form of a yellowish powder with a grain size between 120 and 240 μm. A more in-depth characterization of this raw material was carried out in a previous work (Jiménez-Rosado et al., 2022).

Zinc was incorporated by introducing a salt, specifically zinc sulfate monohydrate ($ZnSO_4 \cdot H_2O$). This salt is commonly used to supply zinc to crops with zinc deficiency (Alloway, 2008). This was provided by Panreac Química S.A. (Spain) in the form of a white powder with a grain size between 130 and 150 μm.

2.2. Preparation of soy protein-based tablets

The processing method of soy protein-based tablets consisted of two stages, following the protocol patented by Jiménez-Rosado et al. (2023a), (2023b). Firstly, SPI was manually mixed with $ZnSO_4 \cdot H_2O$ in a 9:1 ratio. This proportion was chosen based on previous works, where protein-based matrices with incorporated zinc were processed by injection molding (Jiménez-Rosado et al., 2018). The mixture was subsequently compacted using a lab-scale uniaxial compression system (Pilot, Costa Rica). To this end, a pressure of 333, 416 or 776 MPa was applied for 1 min, obtaining cylindrical tablets of 15 mm in diameter and 5 mm in height.

Additionally, some tablets were subjected to a heat treatment (HT) at 50 ºC for 4 or 24 h. This treatment allows to strengthen the structure of the tablet, which can improve its mechanical properties and slow down the release of zinc (Álvarez-Castillo et al., 2018; Jiménez-Rosado et al., 2020).

A process diagram has been included as supplementary information (Figure S1).

2.3. Characterization of soy protein-based tablets

2.3.1. Mechanical properties

The mechanical properties of the tablets were measured by compression tests because they will be the efforts that the systems will mostly have to endure during storage and application. For this, a dynamic-mechanical rheometer (TA Instrument, USA) with a plate-plate geometry of 15 mm in diameter was used. First, strain sweep tests were carried out from 0.002% to 2% of strain at 1 Hz and room temperature (25 ± 2 ºC). From these tests, the critical strain (ε_{crit}, maximum strain supported before irreversible system change) of the different tablets was evaluated. Later, frequency sweep tests were performed between 0.02 and 20 Hz at 65% of ε_{crit} and room temperature (25 ± 2 ºC). In these tests, the elastic (E') and viscous (E'') moduli were studied over the entire frequency range. Furthermore, the elastic modulus (E'_1) and loss tangent ($\tan \delta_1 = E''_1/E'_1$) at 1 Hz were selected in order to facilitate the comparison between the different systems.

2.3.2. Microstructural properties

The structure of the systems could change depending on the pressure applied and the time of exposure to heat, thereby modifying the properties of the tablets. Therefore, the different processed systems were analyzed via Scanning Electron Microscopy (SEM). Previously, a sputter coating with Pd/Au was made to improve the electrical conductivity of the samples and, thus, to improve the quality of the micrographs (Alonso-González et al., 2021). Subsequently, the different systems were observed with a scanning electron microscope Zeiss EVO (Germany) at an acceleration voltage of 10 kV and x100 magnification. Then, ImageJ software (public domain Java image processing program) was used to measure the grain size by a statistical test. The mean grain size was obtained by measuring an average of 100 grains. The uniformity of the systems was also analyzed as the ratio between the standard deviation and the mean grain size.

In addition, the ASTM grain number was also measured, following the ASTM E112–13 standard (ASTM E112–13, 2013). The analysis was performed by adapting the UNE EN ISO 643 standard to the studied materials (UNE-EN ISO 643:2013). Among the different alternatives, the planimetric methods were followed. A 79.8 mm circle was superimposed on the micrograph at x100 magnification. The grains that were completely inside the circle (n_1, x1) and those that intersected its perimeter (n_2, x0.5) were counted. Finally, the index or grain number (G) was obtained from Eq. 1:

$$m = 8 \cdot 2^{G} \quad (1)$$

.

where m is the total number of grains counted and G is the ASTM grain number.

2.3.3. Study of zinc release

The purpose of the studied tablets is the controlled release of zinc. Essawy et al. (Essawy et al., 2016) proposed a method to quickly assess this release. To this end, the systems (0.7 g) are immersed in 300 mL of running water (pH 7, 20 ºC), where the zinc is slowly released. To evaluate the release produced, the conductivity of the medium is measured over time (in continuous mode), which will vary as the concentration of salt in the immersion water increases. The release will end when the conductivity remains constant, thus allowing the measurement of the maximum release time of the different systems.

Furthermore, a study of the release kinetics of the different systems was carried out. For this, two mathematical models, one proposed by Higuchi (1963) and the other by Korsmeyer and Peppas (1983), were used and compared (Eq. 2).

$$L = k \cdot t^{n} \quad (2)$$

where L is the fraction of fertilizer released at time t (measured in conductivity values), k is the release rate constant and n is an exponent that indicates the mechanism by which the release occurs, being always 0.5 in Higuchi's model.

Thus, the value of n provides information about the release kinetics; therefore, if n is 0.5, the release takes place through a Fickian-type diffusion phenomenon (as Higuchi describes). On the other hand, if n is between 0.1 and 0.3, there are several simultaneous processes, none of them being predominant. If n is between 0.5 and 1, the release is due to a non-Fickian or abnormal diffusion mechanism. Finally, when n is equal to 1, the release mechanism depends on the relaxation process of the biopolymeric chains of the protein (Korsmeyer et al., 1983).

2.3.4. Water uptake capacity & soluble matter loss

One of the added values of these systems is their water uptake capacity. The ability to retain water and release it in a controlled manner allows the systems to be used as a source of water. This quality is very useful in farmlands that have difficult access to water, since it reduces the amount of irrigation water required for production (Essawy et al., 2016). To measure this property, each tablet was immersed in 300 mL of distilled water for 24 h, following the ASTM D570–98 standard (ASTM D570–98, 2005). Thus, water uptake capacity (*WUC*) was calculated using Eq. 3:

$$WUC \quad (\%) = \frac{m_2 - m_3}{m_3} \cdot 100 \quad (3)$$

where m_2 is the system weight after water immersion and m_3 is the system weight after water immersion and dry treatment by freeze-drying.

Furthermore, the soluble matter loss (*SML*) of the different systems was measured in order to evaluate the stability of the developed systems upon water absorption. For this, Eq. 4 was used:

$$SML \quad (\%) = \frac{m_1 - m_3}{m_1} \cdot 100 \quad (4)$$

where m_1 is the system weight before water immersion and m_3, as described above, is the system weight after water immersion and dry treatment by freeze-drying.

2.4. Statistical analysis

At least three replicates of each sample were measured to determine the possible deviation of the results for the different techniques used. Thus, the standard deviation was calculated for each parameter using the SPSS 18 statistical package.

3. Results

3.1. Mechanical properties

The compression frequency tests carried out with the different systems are shown in Fig. 1. As can be seen, all the systems had a slight increase in the elastic modulus with frequency. This indicates a certain instability of the systems with respect to the time of application of a given force. Thus, the longer the application time (lower frequencies), the lower the elastic modulus presented by the system. This behavior has already been observed in other similar devices (Jerez et al., 2007) where the storage modulus and the loss modulus of gluten-based bioplastics showed a slight slope, increasing at higher frequencies values.

The pressure and temperature applied to the systems during their manufacture seemed to have a great influence on the mechanical properties of the tablets. Therefore, when only pressure was applied (Fig. 1A), it was observed that a higher compaction pressure led to tablets with a higher elastic modulus. This trend prevailed when a 4 h HT was applied (Fig. 1B), although it disappeared after a 24 h HT (Fig. 1C). Thus, the mechanical properties of the tablets made at 333 and 416 MPa improved, obtaining higher E' values than those of the tablet made at 776 MPa when a 24 h HT was applied. This behavior may be due to the strain exerted on the grains during compression. In this way, a compression at high pressures (776 MPa) exerts a greater plastic strain, which creates a high surface tension in the grains, preventing their consolidation in the HT. However, at lower pressures (333 and 416 MPa), the surface tension generated is lower, allowing the restructuring of the grains during the HT, but only when it is applied for long periods of time (24 h). These results are different from those found in other compressed protein systems, which show changes in the mechanical properties after short heat exposure times (even after 1 h) (Jiménez-Rosado et al., 2019; Lamp et al., 2022). However, it is worth mentioning that such difference lies in the addition of a plasticizer, which facilitates the reorganization of the chains during the application of heat. Thus, long exposures are not required to observe significant changes. Nevertheless, the inclusion of a plasticizer in the studied tablets means that the release of zinc is not controlled, and thus their functionality is lost (Jiménez-Rosado et al., 2020c).

Moreover, E'_1 and tan δ_1 and ε_{crit} are shown in Fig. 2 to improve the comparison between the systems. As can be seen, the critical strain presented was very low, observing that the systems are very rigid, corroborating their strong solid character. There are no significant differences in E'_1 between the systems without HT and those with a 4 h HT, except for the tablet made at 776 MPa, which seemed to worsen even after HT. Therefore, a short period of HT is not enough to produce a significant change in the structure of the material that allows for the improvement of its mechanical properties. Nevertheless, this change is significant after 24 h HT. Thus, it can be inferred that heat is an

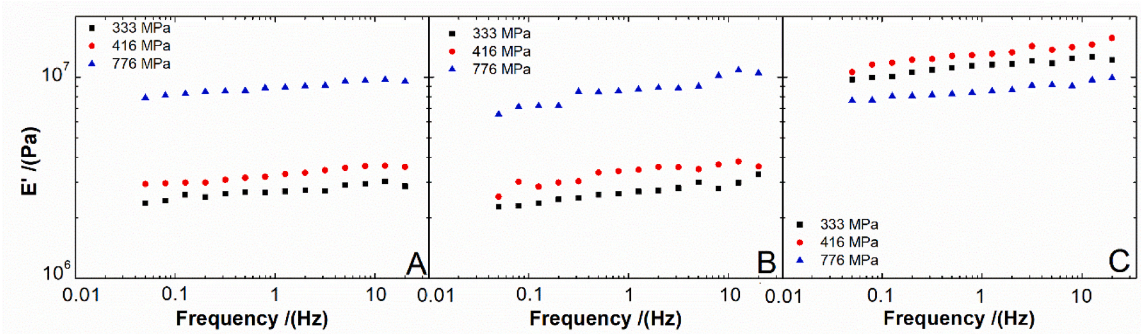

Fig. 1. Compression frequency behavior (elastic modulus (E') vs. frequency) of the tablets at different pressures (333, 416 and 776 MPa) and different heat-treatment times: A: 0 h, B: 4 h and C: 24 h.

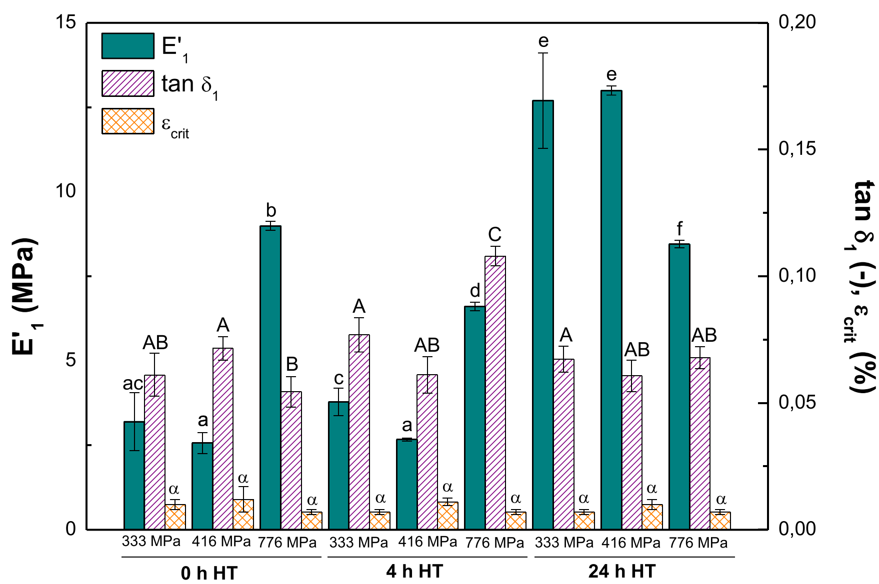

Fig. 2. Mechanical parameters of the tablets at different pressures and heat-treatment times (HT): elastic modulus (E'_1), loss tangent (tan δ_1) and critical strain (ε_{crit}). Different letters show significant differences in the values ($p < 0.05$).

influential parameter in this process, although long exposure times are required for the effects to be noticeable. This may be in accordance with a study carried out by Ye et al. (2006), in which when low temperature and short time were applied, HT had a minimal effect on the modulus which might be due to the polymer's secondary interactions and free volume kinetics (Jansens et al., 2013). On the other hand, pressure has a similar effect on these systems. Thus, a slight increase in pressure (333–416 MPa) during the processing of the tablets did not produce significant changes in the mechanical properties of the systems. However, a greater increase (up to 776 MPa) did cause significant changes. Furthermore, a combined effect of pressure and temperature had significant changes only when the pressure used was low (333 or 416 MPa) and the time of exposure to heat was high (24 h), as was previously explained. Similar results were obtained by (Mo et al., 1999) which found that temperature and pressure where the most significant parameters in the compression molding, causing large variations in the mechanical properties of protein-based systems, although in their case with incorporated plasticizer (Mo et al., 1999). Regarding tan δ_1, its value was below 0.2 in all cases, reflecting the strong solid character of these systems.

3.2. Microstructural properties

Fig. 3 shows the systems both macroscopically and microscopically. Although the systems do not present differences to the naked eye (Fig. 3A, 3B and 3C), these differences are more appreciable at the microscopic level (Fig. 3', 3'' and 3'''). A more homogeneous surface was generally observed when the applied pressure was higher and the HT time was shorter. This behavior could be due to the higher surface tension generated at higher compaction pressures, which makes the surface more homogeneous and with fewer cracks. These results could explain the better mechanical properties previously observed at higher pressures and shorter time. On the other hand, a longer HT allowed the grains to be reorganized, losing the homogeneity given by the initial compaction. These differences can be better appreciated in the study of grains of the tablets observed in Fig. 4.

In general, a similar effect was observed for the three pressures studied (333, 416 and 776 MPa). The application of a HT at 50 ºC increased the homogeneity of the structure obtained when the applied time of the treatment was 4 hours, according to the values of uniformity of the grain size shown in Fig. 4A', 4B' and 4 C'. However, when the HT was performed for 24 h, greater heterogeneity in the grain size of the structures was achieved. This behavior was also shown by the grain size distribution (Fig. 4A'', B'' and C'').

The grains present in the structure of the bioplastics were analyzed in two different ways. Firstly, the ASTM grain number (ASTM E112) was obtained. The ASTM grain number is a qualitative way to measure the grain size of a sample. The higher the ASTM grain number, the higher the number of grains and, therefore, the lower the grain size. The values exhibited two different trends depending on the compression pressure

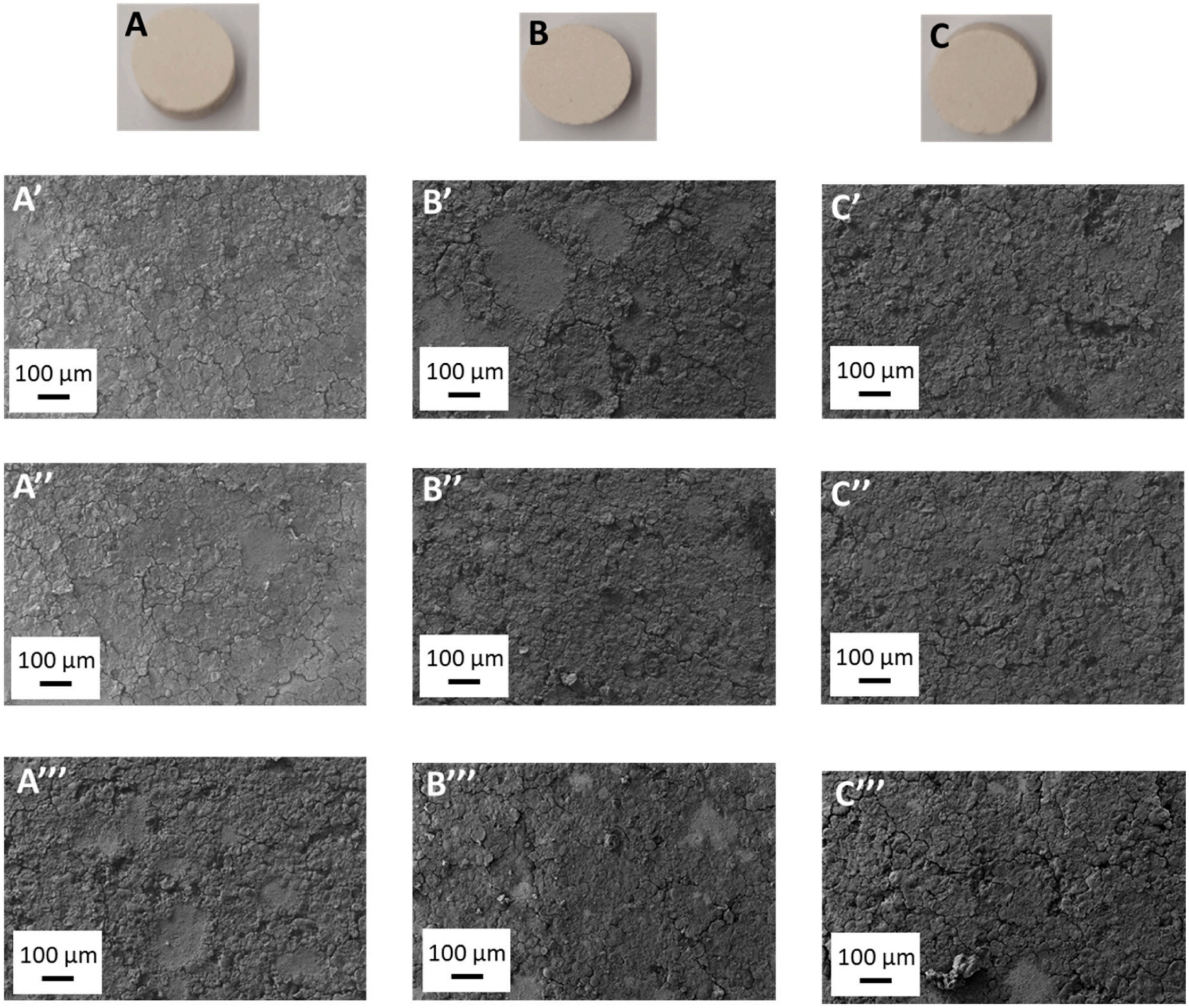

Fig. 3. Macrographs (A, B, C) and micrographs at 0 h of heat treatment (HT) (A', B' and C'), 4 h HT (A'', B'' and C'') and 24 h HT (A''', B''' and C''') of the tablets at 333 (A, A', A'' and A'''), 416 (B, B', B'' and B''') and 776 MPa (C, C', C'' and C''').

used, since the use of a compression pressure lower than 416 MPa induced a higher ASTM grain number when the specimens were submitted to a heat treatment of 24 h. However, the use of a higher compression pressure (776 MPa) induced no significant differences in the specimens.

Regarding the mean grain size, the evolution of this parameter followed a similar trend. On the one hand, for the samples prepared at 333 and 416 MPa, the average grain size decreased when the systems were subjected to a heat treatment of 24 hours. However, the mean grain size obtained by the system made at 776 MPa was similar, regardless of the heat treatment carried out. These results are in line with those obtained in the studies carried out by Barbato et al. (2008) and Nečina and Pabst (2020), in which a higher temperature led to lower values of grain size. Regarding the system developed at 776 MPa, it did not follow the same trend, probably due to the high pressure used for its production, giving rise to a more compact system that prevents the modification of its structure.

The evolution of the mean grain size can explain the mechanical properties obtained by the systems. According to previous studies, a decrease in grain size leads to an increase in mechanical properties (Justo et al., 2020; Sadeq et al., 2020; Wang et al., 2020). A similar effect was observed with the bioplastics obtained in this study, since, for the systems produced at 333 and 416 MPa, the elastic modulus values increased when they were processed with a 24-hour dehydrothermal treatment (coinciding with the decrease in the mean grain size), while the system at 776 MPa did not show significant variations in E' values. Therefore, the higher pressure used did not allow the reorganization of the structure with a heat treatment at 50 ºC; thus, it may be necessary to increase the temperature in order to achieve this end.

3.3. *Study of zinc release*

The controlled release of zinc is the main property of these tablets. To evaluate this capacity, Fig. 5 shows the zinc release of the different studied systems to the water. As can be seen in Fig. 5A, there was a significant difference in release at the compaction pressure of 776 MPa when only pressure was applied to the systems. Thus, this system had a faster release (with a greater slope), reaching the stability of the measured conductivity (maximum release) in a shorter time (420 min) than the other two systems (540 min). However, only a high increase in pressure generated this change in release, as there were no significant differences between the 333 and 416 MPa tablets. These results are consistent with those obtained for the mechanical properties, where no significant differences were observed between these systems. In this sense, it seems that the higher surface tension of the grains of the systems processed at 776 MPa weakened the protein-salt interaction, which, together with the lower uniformity of the system, allowed water to penetrate more easily inside it and drag the zinc with it. Applying a HT to the samples made the differences found between the systems disappear (Fig. 5B and 5C). As the uniformity of the systems processed at

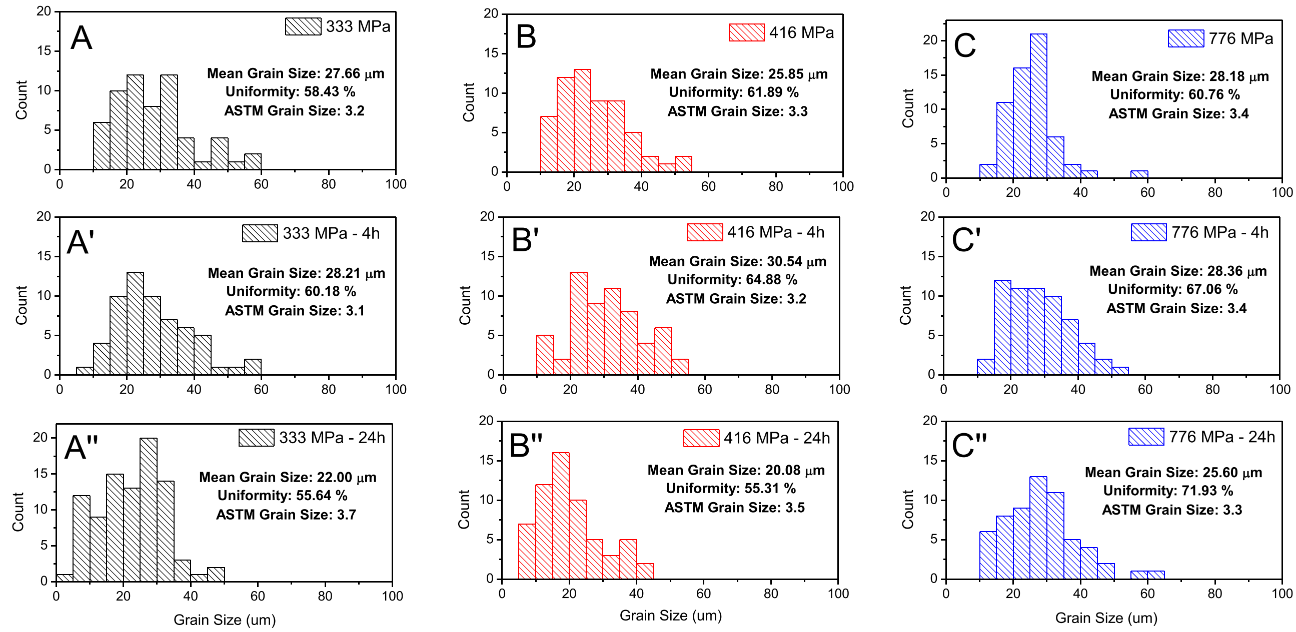

Fig. 4. Grain distribution of the tablets at different compaction pressures: 333 (A, B and C), 416 (A', B' and C') and 776 MPa (A'', B'' and C''), and different heat-treatment times: 0 h (A, A' and A''), 4 h (B, B' and B'') and 24 h (C, C' and C'').

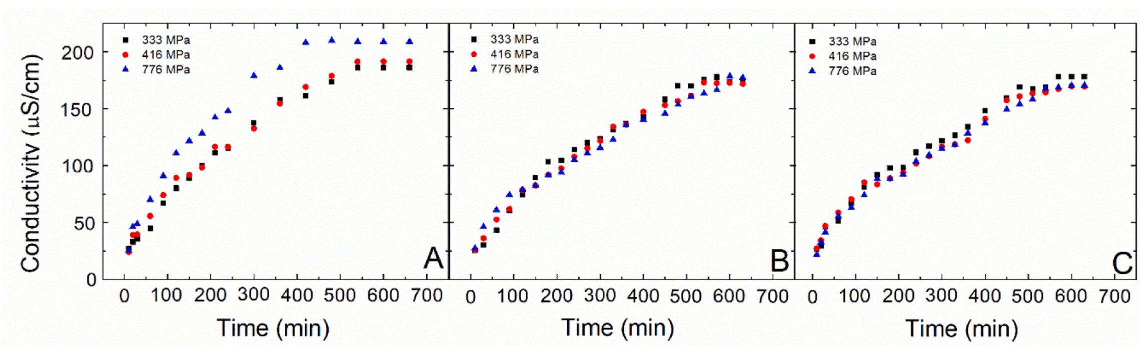

Fig. 5. Zinc release tests in water of the different tablets at 333, 416 and 776 MPa at different heat-treatment times: 0 h (A), 4 h (B) and 24 h (C).

776 MPa was still lower than that of the other tablets, it seems that the HT only allowed improving the protein-salt interaction, making it more difficult for them to be dragged by the water. However, the HT in both exposure times (4 and 24 h) did not cause an improvement in the maximum release time, improving only in the system developed at 416 MPa (Table 1). Comparing these systems with others used in the literature for the same purpose (Jiménez-Rosado et al., 2020d, 2020a), it is observed that this processing method allows the products to have a slower controlled release, with a maximum release time over double the one obtained in the present study (300 vs. 700 min). This fact is favorable for their use in horticulture, since a release of zinc is necessary during the entire germination and growth time of the crop, allowing it to be used in a greater variety of products (Hanafi et al., 2002). This modification in the results is due to the different structures observed in the materials, since those studied in the literature present a more porous structure and with poorer mechanical properties (lower elastic modulus), thus facilitating the release of the micronutrient.

The release produced by each matrix was modeled using the Higuchi (H) and Korsmeyer-Peppas (K-P) mathematical models, in order to improve the understanding of the processes that occur during zinc release. Fig. 6 shows that both models are adequately adjusted to the experimental data obtained, with the release rate constant (*k*) and the exponent *n* being those indicated in Table 1. As can be seen, the K-P model generates less uncertainty in the results (R^2 closer to 1) in most cases. However, the value of the exponent *n* is only slightly greater than 0.5. These results may be due to the fact that the formation of channels within the system, which are necessary for the release of zinc, is accompanied by the release of the air trapped in the internal pores, causing the rupture of the segments of the protein matrix, which weakens its cohesive capacity, thereby forming cracks. Thus, the release

Table 1
Parameters of Higuchi and Korsmeyer-Peppas models of tablets processed at different pressure and exposure time of heat treatment (HT). Maximum release time of micronutrient in the systems.

HT time	Systems (MPa)	Higuchi (H)		Korsmeyer-Peppas (K-P)			Maximum release time (min)
		k	R^2	k	n	R^2	
0 h	**333**	7.76^{a}	0.983	5.50^{A}	0.54^{α}	0.986	570^{I}
	416	8.00^{b}	0.982	5.93^{B}	0.54^{β}	0.987	540^{II}
	776	9.88^{c}	0.980	8.33^{C}	0.53^{γ}	0.985	600^{III}
4 h	**333**	6.98^{d}	0.984	6.61^{D}	0.52^{δ}	0.986	570^{I}
	416	6.98^{d}	0.984	7.20^{E}	0.50^{γ}	0.984	600^{III}
	776	6.90^{d}	0.985	6.05^{B}	0.53^{η}	0.987	570^{I}
24 h	**333**	7.30^{a}	0.984	6.61^{D}	0.52^{δ}	0.986	570^{I}
	416	7.15^{d}	0.984	5.73^{E}	0.54^{ζ}	0.984	600^{III}
	776	7.00^{d}	0.984	7.42^{B}	0.50^{η}	0.987	600^{III}

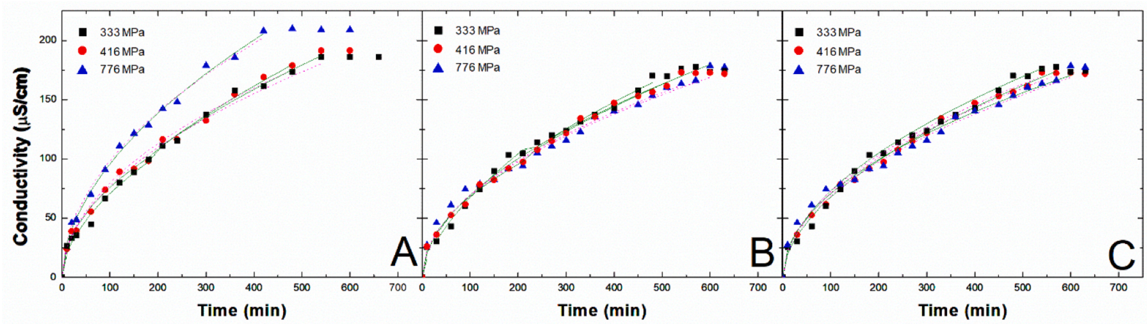

Fig. 6. Higuchi (H) and Korsmeyer-Peppas (K-P) modulization of the tablets at different compaction pressures: and different heat-treatment times: 0 h (A), 4 h (B) and 24 h (C).

of zinc from the tablets occurs mainly through a Fickian-type diffusion process through the channels formed in them which has been also observed in other study carried out with starch by Chiaregato and Faez (2021). However, although this is the predominant release process, it is not the only one present, making the K-P model better than the H model to fit the obtained results. The other less predominant processes could be the disintegration of the protein matrix and the solubility of the salt and protein in the medium, as anticipated in other works (Fernández-Espada et al., 2016).

The formation of cracks in the tablets during zinc release is demonstrated in the macro and micrographs obtained from the systems before and after the release tests (Fig. 7). This degradation is due to the morphological and mechanical characteristics of the different grains that make up the tablets, which are largely due to the formation processing method used. Thus, during processing, micropores are produced, which allow the absorption of water, spreading to form cracks and cavities through which diffusion occurs.

3.4. Water uptake capacity & soluble matter loss

Finally, the water uptake capacity (*WUC*) of the different systems was measured as an added-value property of them. As can be seen in Fig. 8, there were no significant differences between the *WUC* of the different tablets. Thus, neither the compaction pressure nor the HT time had an impact on this capacity. The obtained *WUC* (approximately 130%) did not reach the superabsorbent values (>1000%) obtained in

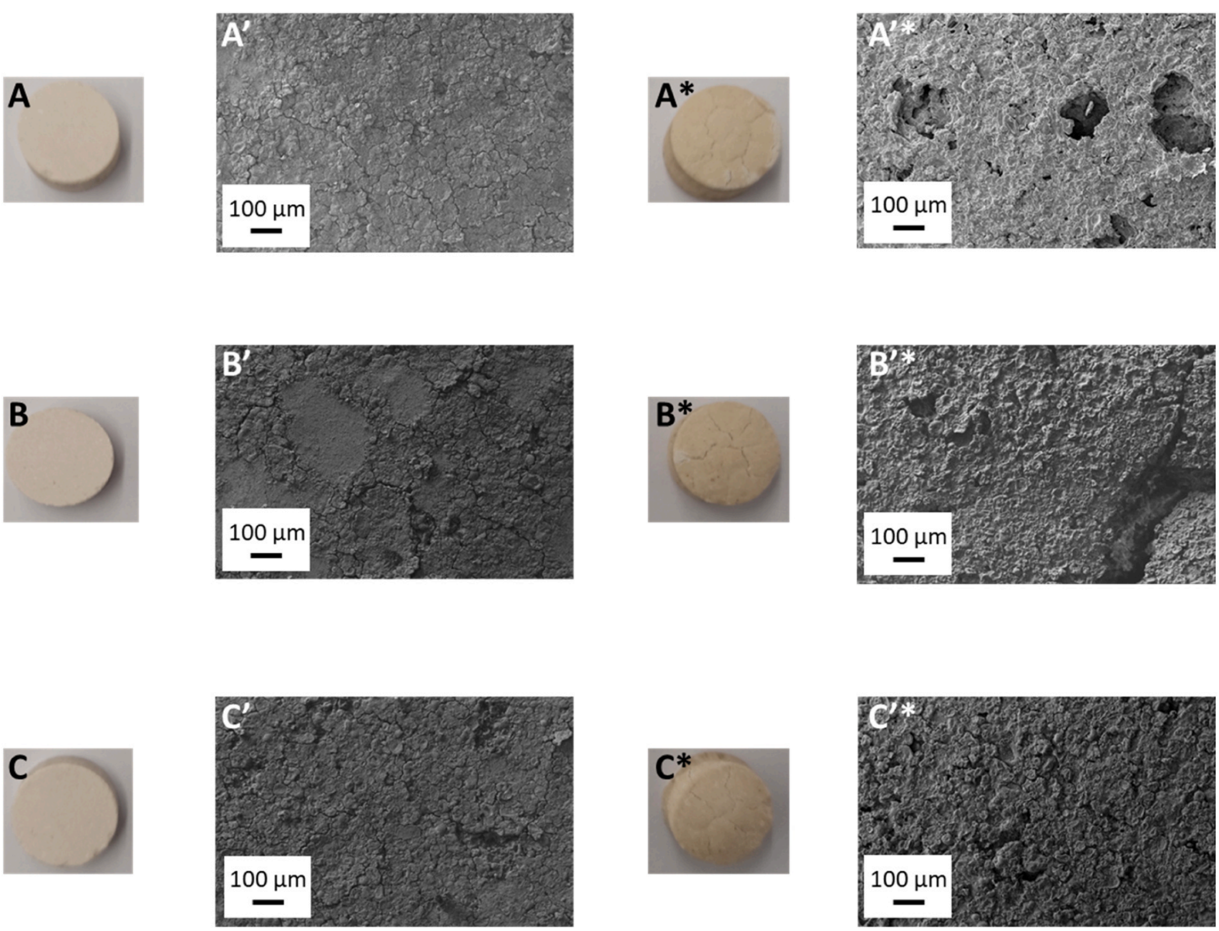

Fig. 7. Macrographs (A, B, C, A*, B* and C*) and micrographs (A', B', C', A'*, B'* and C'*) of the tablets before and after (*) the release tests at different compaction pressures: 333 (A), 416 (B) and 776 MPa (C).

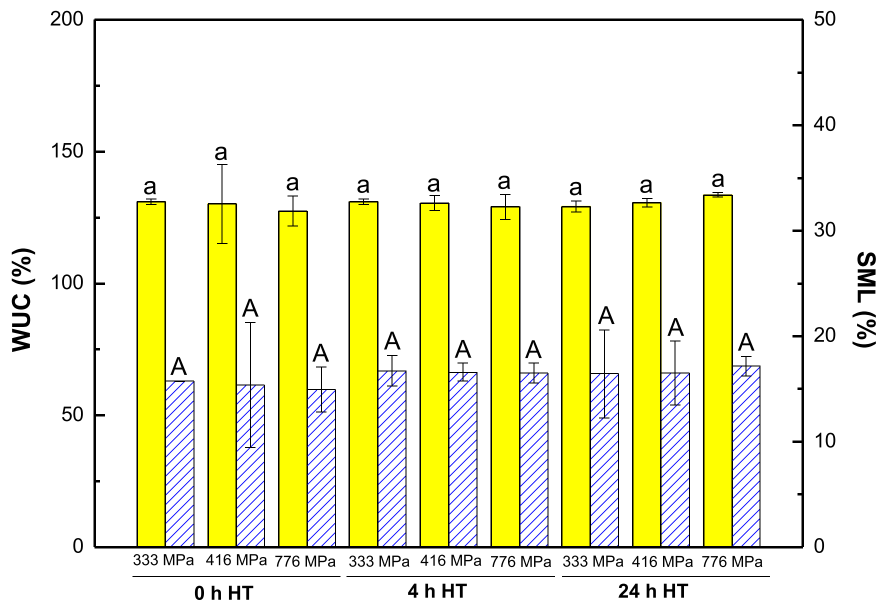

Fig. 8. Water uptake capacity (WUC) and soluble matter loss (SML) of the tablets processed at different compaction pressures and heat-treatment times (HT).

other systems designed for the retention of water in crops (Cuadri et al., 2017), possibly due to ionic forces generated when the salt dissolves in the water and to the difficulty of the compressed protein matrix to swell (Ma et al., 2011; Sadeghi and Hosseinzadeh, 2008), achieving values close to those of other matrices made for the same purpose (Jiménez-Rosado et al., 2018). However, according to Messa et al. (2016), who obtained equilibrium values of 192%, these are optimal (150–200%) for the supply of water in horticulture, thus increasing the value of this product.

On the other hand, soluble matter loss (*SML*) indicates that, after 24 h of exposure to water, all the salt present in the systems (10%) is lost, due to its release, which was already estimated at 7–9 h in the release tests. However, a percentage of the protein matrix was lost (approximately 6%), which is in line with the results explained above, suggesting that the release of salt to the medium was not produced only by diffusion, but also through the loss of part of the protein matrix, although to a lesser extent. This result could be an advantage over other thermomoulded systems where it is necessary to incorporate glycerin. Glycerin is easily released from the system, modifying its structure and properties, making the controlled release of the micronutrient difficult (Jiménez-Rosado et al., 2020b).

4. Conclusions

To sum up, soy protein-based tablets have demonstrated their high potential to supply zinc to crops in a controlled way. In this way, a significant amount of zinc (116 g Zn/kg product) was incorporated into the matrix by compression molding (a low-cost process). The production rate could be 60 tablets/h in a continuous process, with means a production price of 0.464–4.424 € per 100 tablets (supplementary information). All this would improve their commercialization.

All the tablets showed the same water uptake capacity (130%) and an optimal and controlled release of zinc (9–9.5 h in water). Thus, compaction pressure only defined the biodegradability time of the product, and it could be modified to fit the growth time of the crop.

Therefore, these soy protein-based tablets with zinc incorporated are a potential product for commercialization. Nevertheless, it is necessary to carry out release tests in the farmland in order to better define their zinc release, as well as their assimilation by plants.

CRediT authorship contribution statement

Romero Alberto: Writing – review & editing, Validation, Supervision, Resources, Methodology, Funding acquisition. **Perez-Puyana Victor M:** Writing – review & editing, Writing – original draft, Validation, Software, Methodology, Formal analysis, Data curation, Conceptualization. **Rubio-Valle José Fernando:** Writing – original draft, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Castro-Criado Daniel:** Writing – original draft, Investigation, Formal analysis, Conceptualization. **Jiménez-Rosado Mercedes:** Writing – original draft, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.indcrop.2024.118261.

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