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Easy method for obtaining slow-release biofertilizer enriched with marine plant residues

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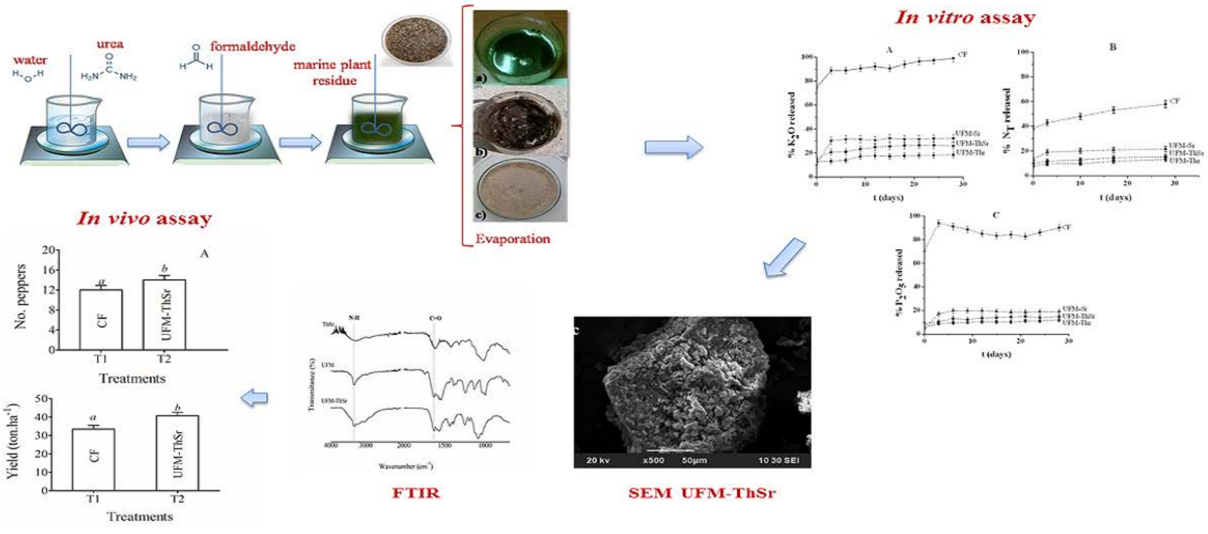
Abstract

The increase in the use of conventional fertilizers, joined to their low efficiency, pose an economic, social and environmental problems. Slow -Release Fertilizers (SRF) emerges as a solution to this problem by providing nutrients to the plant in an efficient and prolonged over time. In this work, SRF formulations were developed by incorporating industrial waste from marine plants, *Thalassia testudinum* (Thr), *Syringodium filiforme* (Sr), encapsulated with a matrix based on urea-formaldehyde-based matrix (UFM). Macronutrients and micronutrients (N, P, K, Cu, Co, Mn, Fe, Zn, Ni and Ca) analysis indicated that they have a suitable composition to the use as organic fertilizers. In vitro studies showed that the macronutrients released from the proposed system were delayed considerably compared to the conventional mineral fertilizer (CF). The structural characterization of the matrix prepared (UFM-ThSr) was investigated using Fourier Transform Infrared Spectroscopy (FTIR). The Morphological observation by scanning electron microscopy (SEM) revealed a high surface irregularity, with cavities.Finally, the efficiency of the biofertilizer (UFM-ThSr) was proved in terms of crop yield in pepper crops (*Capsicum annum L.*).

Graphical Abstract



1. Introduction

In the recent decades, the development of Slow Release Fertilizers (SRF) has become a focus for agriculture [1,2].SRFs offer wide advantages over conventional mineral fertilizers, and they provide adequate amounts of nutrients during the plants growth process. The SRF extending the time in which the dose is effective and avoids the fast release of nutrients in the environment [3,4]. Consequently, the frequency of fertilization could be reduced, as well as the environmental problems associated to the use of conventional mineral fertilizers such as immobilization, denitrification or leaching [4-7].

Products based on urea-formaldehyde (UF) are of special interest, amongo ther products proved for controlled release of nitrogen into the soil. Moreover, UF-based products belong to the first group of materials developed for the slow release of nitrogen [2,8]. Differentstudies have been reported that nitrogen release rates from UF and urea were similar in agriculture [9].Furthermore, patents have also been described a SRF formulations of urea-formaldehyde [10].Some of them refer to a product with a liquid UF composition [11];others define formulations of urea-formaldehyde polymers in the form of dry powder [12], and athird group refers to granular fertilizers produced by the reaction between urea and formaldehyde to give a solidified resin as a final product [13].However, the production cost of these materials is high, due to the rigor in the reaction conditions (pH, temperature, U/F ratio, use of catalysts.).

Another patent describes obtaining a stable low molecular weight polymer suspension based on urea-formaldehyde for the encapsulation of a conventional commercial fertilizer [14].This invention proposes a method to obtain an SRF with a lower production cost. Since the process does not present a high complexity since the time used, the molar ratios of the monomers and their obtaining at room temperature, make the described method more economically attractive. The use of this polymeric urea-formaldehyde suspension as a natural coating for active ingredients could be original solution for agriculture.

Liquid extracted from seaweed and marine plants constitutes a new generation of natural fertilizers (biofertilizers). They have been shown to be a nutritional source, promote rapid germination of seeds, and increase yield and resilience capacity of many crops [15]. Furthermore, the effects of these liquid extracts on vegetables, fruits, flowers, medicinal plants, and turf have been well investigated [16].The use of these extracts is given by the presence of macro and micronutrients, phytohormones, polyphenols, polysaccharides, vitamins, proteins [17,18]. Although the stimulation and growth mechanisms are not totally known. Nowadays, seaweed-based fertilizers have reached an important place in organic agriculture [19,20]. Some of the commercial liquid extracts obtained from seaweed are Acadie from Ascophyllumnodosum, AgroKelpfrom Macrocystispyrifera, Kelpak from Ecklonia maxima and Seasol from Durvilleapotatorum [21]. However, a direct and prolonged application of these extracted liquids could lead to some inconveniences. The high salt content in seaweed (Na^+, Cl^-, K^+, Ca^{2+}, etc.) can contribute to the development of saline soils and increases the salt amount in plant tissues[17]. In addition, anaerobic decomposition of sulfated organic compounds presented in seaweed leads to the production of sulfides, which are toxic to the plants [22]. Furthermore, typical polysaccharides coming from seaweed and marine plants (alginates, ulvans, carrageenans, fucoidans) expose new and less biodegradable compound underaerobic conditions [23]. In this context, biological fertilizers coated could be the main solution to overcome the limitations cited before by regulating the release rate of nutrients with the crops uptake.

The Cuban island shelf is a territory for many species of macro algae and marine plants. Among the most abundant marine plants in Cuban coasts are *Thalassia testudinum*, *Syringodium filiforme*, which naturally coexist in symbiosis. Theses pecies have a great diversity of biologically active compounds (polyphenols, flavonoids, polysaccharides, lipids, proteins, chlorophylls) [24,25]. Many of these metabolites display antioxidant, anti-tumor, anti-inflammatory and anti-diabetic properties, among others. Therefore, they are used in the production of a liquid extracted the National Cosmetic Industry [26]. From this industrial process, a solid waste is generated and still containing compounds that could be of interest for the agricultural industry such as macro and micronutrients, polyphenols and flavonoids. As far as we know, *T. testudinum* and *S. filiforme* as biofertilizers was never been investigated. The incorporation of marine plant industrial waste to SRF formulations gives an ecological perspective to the development of the agricultural industry. This methodology provides an outlet for algae and marine plant residues from waste industry. In addition, it can be applicable to the large biomass of algae and marine plants that were accumulated on the coasts.

The aim of this work was the preparation of slow-release formulations (UFM-ThSr), following an easy microencapsulation method (solvent extraction and evaporation). For this purpose, a biodegradable matrix based on urea-formaldehyde (UFM) was used, in which the industrial waste of marine plants (*T. testudinum* + *S. filiforme*) was incorporated. All this, allows us to provide an agro-ecological solution through the sustainable reuse of natural sources. At the same time, the rational use of the materials and resources open an opportunity to wards the closed-cycle industry in this productive sector of the country.

2.Methodology

2.1 Determination of nutrients in marine plant residues.

2.1.1 Quantitative macronutrientanalysis (NPK).

For the analytical determinations and preparation of the formulations, the marine residuesdried in the sun for 30 minutes wereused. These residues are ground in a ball mill (JISICO, J-BM1-S).1 gram of the marine residues was weighed for each determination. Total nitrogen (N_T) was analyzed according to Kjeldahl method [27]. The analysis of water-soluble phosphorus content (P_2O_5) was performe dusing the colorimetric technique at a wavelength of 450 nm in an UV spectrometer/Visible brand GENESYS 20 UV SPECTRONIC [28]. Potassium (K_2O) determination was carried out in Atomic Absorption Spectrophotometer (PG Instruments, AA500), at a wavelength of 766.5 nm [29].

2.1.2 Quantitative micronutrientanalysis.

10 gram of each sample was taken to carry out the digestion process.These processes were carried out in a 250 mLbeaker, 4 mL of concentrated perchloricacid (HClO4) were added and it was left to stand for 24 hours.Next, 8 mL of concentrated nitricacid (HNO3) were added and after 30 minutes of rest, it was placed on a heating plate until the concentration of salt residues.It was allowed to cool, filtered and taken up in 25 ml of distilled water for analysis.All reagents used were pure for analysis (Merck). The calibration standards series were prepared from standard solutions of 1000 mgL^{-1} [30]. Samples were analyzed by an Atomic Absorption Spectrophotometer (Perkin-Elmer, AAS 2280).

2.2 Synthesis of UFM matrix and microencapsulation of marine plant residues

The preparation of UFM matrix was carried out following the procedure described by González [31]. The synthesis was carried out by means of a polycondensation reaction between urea (Panreac) and formaldehyde (Merck 37%). The molar ratio used of urea/formaldehydeis 0.5/1. The reaction was developed at room temperature under mechanical stirring (MAGNESTIR 1250; S5560-1), at 700 r.p.m until reaching a viscosity of ~ 1.8 $g.cm^{-1}.s^{-1}$. At this time, the ground residues of marine plants (5g) were added to the formulation of UFM prepared for their microencapsulation. Later, the obtained systems UFM-Sr, UFM-Thr and UFM-ThSr were dried at room temperature. The matrix UFM was synthesized similarly, but without marine plant residues. The theoretical total nitrogen value for all the proposed systems are: 46.57 % (UFM); 38.80 % (UFM-Sr); 38.83 % (UFM-Thr) and 38.90 % (UFM-ThSr).

2.3 In vitro study of macronutrients (NPK)

In vitro studies of macronutrients were performed in an ideal environment (water); 5g of the formulations (UFM-Sr; UFM-Thr and UFM-ThSr) and CF were added in 500 ml of distilled water, with a stirring speed of 100 rpm. Small volumes (5 ml) of the aqueous phase were collected every 3 days, keeping the total volume constant during the test period (25-30 days) [8, 32]. Each aliquot was diluted at 100 ml of distilled water to determine the percentage of N_T, K_2O and P_2O_5 released in the solution, according to the methodology described in section 2.1.1. A CF without microencapsulating was used as reference. The release profile of each macronutrient versus time were calculated and represented graphically.

2.4Characterization of UFM-ThSr formulation and UFM matrix.

2.4.1 Fourier TransformedInfrared (FTIR) Spectroscopy

FTIR spectra were obtained from a FTIR THERM NICOLET Nexus-670 spectrophotometer. Each spectrum was recorded in the range of 4000 to 500 cm^{-1}. For the analysis, 5 mg of sample and 95 mg of KBr were ground at the same time in an agate mortar until obtaining a fine powder. The spectra were recorded with 32 scans and a resolution of 2 cm^{-1}. Before meas uring the spectra, the signal was corrected for the presence of carbondioxide and water in the atmosphere.

2.4.2 Scanning ElectronicMicroscopy (SEM)

Samples were coated with a thin layer of gold (20 nm) before being observed at 20 kV, in the scanning microscope (JEOL-5600 LV).The analysis allowed to have details of its morphology and surface.An approximation of the UFM-ThSr particle size was performe dusing Image J software.

2.4 In vivo study

Experiments were developed in the crop of peppers *Capsicum annuum L.* hybrid variety of Liliana Dimitrova Horticultural Research Institute. This islocated in the municipality of Quivican, south of the province of Mayabeque, Cuba at 22° 23N and 83° 23W and at a sealevel of 68m. The culture was established in a typicalred ferralite soil or Ferrasol Rhodic in correlation with the World Reference Base for Soil Resources [33]. The maximum, minimum and average temperatures were 35.5, 22.87 and 28.69 °C while the relative humidity was 67.73%. The studies were developed in a model A-12 grow house.Two different treatments were applied taking into account the nutritional requirements of the crop.

- T1:Conventional mineral fertilizer, CF (NPK-14-4.7-11.7) at a rate 95.5g/m^2 as control, with two applications during the production cycle 60 days [34].
- T2:Treatment with UFM-ThSr formulation at a rate 40g/m^2, with a single application during the production cycle 60 days.

The variables evaluated during the trial period were: number of peppers per plant and agronomic yield expressed in tons per hectare.

2.5 Statistical analysis

All statistical processing was developed using GraphPad Prism version 5.00 software for Windows [35]. *In vitro* study, the variance analysis test (ANOVA) was carried out, followed by Dunnett's test to determine if there are significant differences between microencapsulated formulations and CF at 30 days ($p < 0.05$). In the *in vivo* study, a Student-Mann-Whitney test was used to define if there are significant differences between CF and microencapsulated formulation (UFM-ThSr) in terms of the agronomic parameters evaluated ($p < 0.05$). Two years of study with the same behavior were taken into account. The means of the number of fruits per plant and yields during this period of time are presented.

3.Results and Discussion

3.1 Macro- and micronutrient characterization in marine plant residues

Table 1 show macronutrients NPK percentages in the marine plant residues studied. The comparative analys is suggested that there is a variation of marine plants residues in terms of macronutrients. Percentages of NPK in ThSr residue (4.52%, 0.170% and 2.11%) were higher when compared to Thr and Sr residues. The lowest percentages of NPK were recorded in Sr residue (3.80%, 0.075% and 0.96 %). The macronutrients (NPK) are important for the growth, photosynthetic capacity and chlorophyll synthesis in plants [36-39].

Table 1:Macronutrient composition in the studiedresidues.

Marine plant residues	N_T(%)	P_2O_5(%)	K_2O(%)
Sr	3.80	0.075	0.96
Thr	4.12	0.130	1.24
ThSr	4.52	0.170	2.11

Table 2 shows the results of micronutrient Cu, Co, Mn, Fe, Zn, Ni and Caanalysis in marine plant residues. The micronutrients analysis showed that the concentration of the elements varies with marine plants residues. Concentrations of Fe, Mn, Zn, Ni and Co (1069-10mg.kg^{-1}respectively) were higher in ThSr residue compared to Thr and Sr residues and Cu concentration was equal in ThSr and Thr residue (18mg.kg^{-1}). The concentration of Fe was highest in all residues. In ThSr residue micronutrients concentrations decrease in the following order : Fe>Mn >Zn>Ca>Cu=Ni>Co while in Thr the sequence is Fe>Mn>Zn>Cu>Ni>Ca>Co. In Sr residue, the following sequences were observed: Fe>Mn>Zn>Cu> Ni>Co>Ca. In all cases (ThSr, Thr and Sr), Fe concentration was the highest. Previous published work assumes that these elements are more easily assimilated by the plants because of their use in photosynthesis [40].

Table 2: Composition of micronutrients in marine plant residues.

Marine plant residues	Cu	Co	Mn	Fe	Zn	Ni	Ca
	(mg.Kg^{-1})						
Sr	20	7	43	443	32	13	5
Thr	18	9	96	1000	36	15	10
ThSr	18	10	105	1069	67	18	23

The results of the analysis of the content of micronutrients presented here (Table 2), are in the range of adequate concentrations that micronutrients must present for optimal crop development [41].

Investigations suggestthat the metabolic condition and lifecycle stage of the individual species might influence macro and micronutrients uptake and accumulation [40]. Moreover, many factors chemical, physical and biological environment could influence the nutrient content in marine plants [41].

The fact that we found highest macro and micronutrients in ThSr residue might be consequence of contribution of the *T. testudinum* and *S. filiforme* species at the elemental composition of this residue.These results confirm the potential of seaweed and marine plants for agriculture, and justify the increase in their use in recent years. The use of conventional mineral fertilizers is avoided with these marine plant residues that are not harmful to the environment due to their biodegradability and non-toxicity [42].

3.2 Synthesis of UFM matrix and microencapsulation of marine plant residues

UFM matrix wasobtained by a step-polycondensation reaction, where formaldehyde reacts with hydrogen atoms of amine (urea) to form terminal methyl groups, which forms methylene bonds after successive condensation reactions between hydroxyl groups of methyl and hydrogen of urea. Importants aspects for obtaining short or long chains are the conditions for their synthesis (pH, temperature, reaction time, urea/formaldehyde ratio, dilution and catalyst addition).

In our study, the synthesis conditions allowed to obtain a stable polymer solution with oligomer mixture. Consequently, the matrix maintains sufficient hydrophilicity to produce a solution, which allows modulating the release of the microencapsulated material.

According to the American Association of Plant Food Control Officials [43], SRFs are divided into three groups: products formed by short polymerchains (2-4 ureaunits per molecule), intermediate chain polymer products (4-6 units of urea per molecule), and long chain polymer products (6-8 units of urea per molecule) [44]. According to what has been reported in the literature [45,46], the results of section 3.3 could indicate that this UFM matrix is mainly formed by chains of short and medium length of methylene-urea.This will favor the nutrient release processes from the matrix. The different stages for obtaining the final product UFM-ThSr are presented in Figure 1 (a, b and c). The same procedure was developed with the rest of marine plant residues.

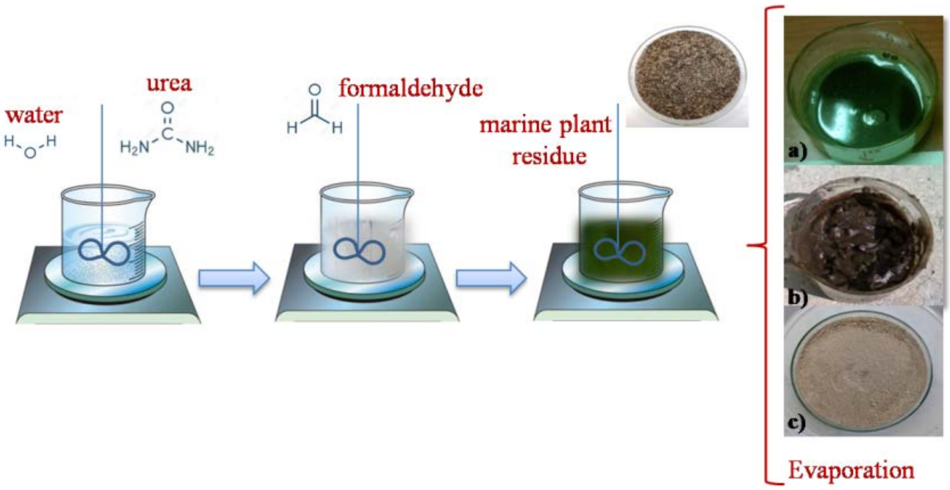


Figure 1: Synthesis scheme from the UFM matrix and the ThSr residue, photograph of the final product (a), after two hours (b) final product (UFM-Thsr) after total solvent evaporation (c).

3.3 In vitro study

Figure 2 shows macronutrient (K_2O, N_T, and P_2O_5) release profiles of the microencapsulated formulations obtained (UFM-Sr, UFM-Thr and UFM-ThSr) and of CF (NPK 14-4.7-11.7) over a 30-day period. The percentage of macronutrients released in UFM-Sr, UFM-Thr and UFM-ThSr was lower compared to CF at 30 days. It can be appreciated that potassium is the fastest released element among all macronutrients (18-32%), due to its high solubility, followed by nitrogen (18-26%) and phosphorus (12-20%). It is observed that the CF incorporates a large part of these macronutrients into the solution almost immediately. This could be explained by the barrier character of the UFM matrix that prevents the rapid release of macronutrients into distilled water. Significant differences were observed between the macronutrients percentage released in all microencapsulated formulations and in CF ($p < 0.05$). The following sequence shows, in decreasing order, the slow-release behavior in the formulations and the matrix: UFM-Sr<UFM-ThSr<UFM-Thr<FC. The differences in the release rates between the microencapsulated formulations obtained could be explained by the macronutrients content differences in Sr, Th and their mixture.

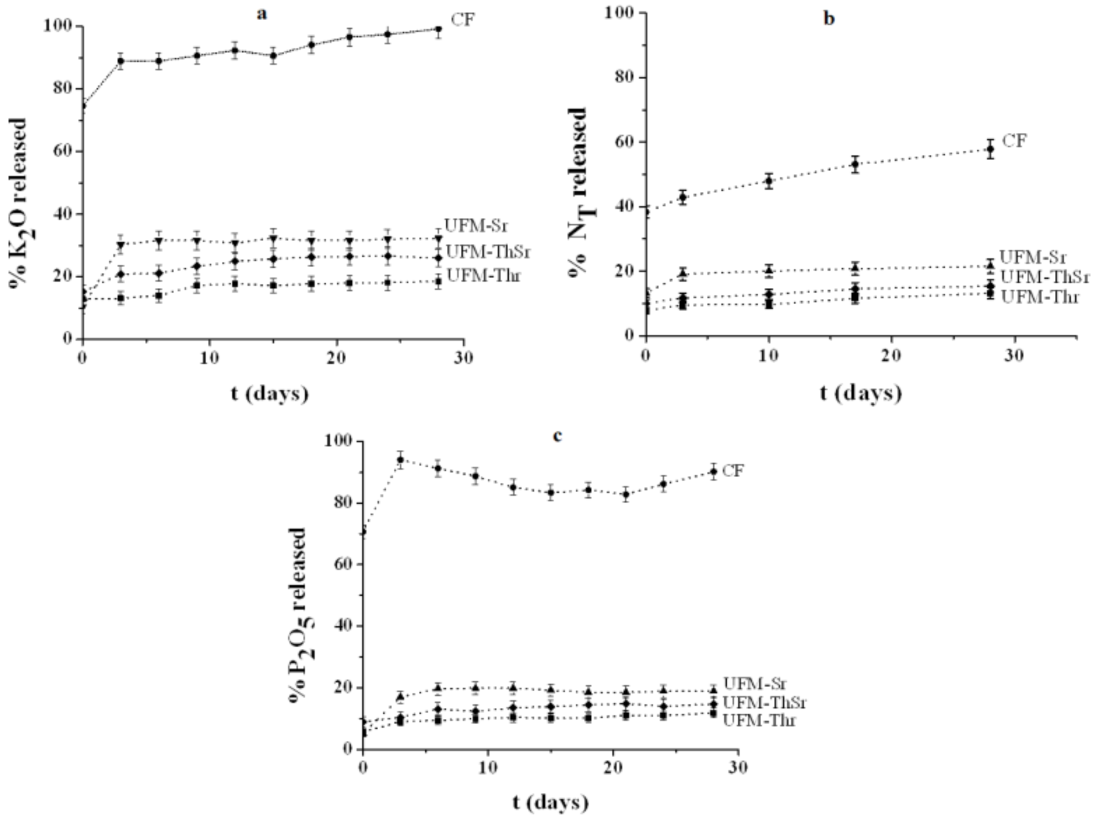


Figure 2: Release behavior in aqueous medium of a) K_2O, b) N_T, and c) P_2O_5 in the CF and in the formulations obtained (UFM-Sr; UFM-Thr and UFM-ThSr).

In general, the graphs show a first stage of low macronutrient release and a second, after 10 days, where the release remains constant. In all the graphs, an initial release of macronutrients at $t = 0$ is observed in all microencapsulated formulations. The cause of this phenomenon could be related to the presence of non-microencapsulated macronutrients on the surface of the matrix (UFM), which is known as the “burst effect” [47,48]. Previous studies described the first stage release of fertilizers that are typically characterized by initial release “burst” followed by slow release [32,49,50]. The European Standardization Committee (ESC) states that a SRF should not release more than 75% of its nutrients in 28 days, at room temperature[3,5]. All the microencapsulated formulations tested showed and NPK release of less than 75% at 30 days of the study. This fact demonstrates that our formulations meet the requirements of an SRF.

3.4 Physical-chemical characterization of the product.

The physical-chemical characterizations were carried out in the UFM-ThSr formulation, taking into account that ThSr residue is the most abundant, and also that it presents the highest macro and micronutrient values as shown in the previous section 3.1.Furthermore, this formulation presented lower macronutrient release compared to CF.

3.4.1 FTIR Spectroscopy.

FTIR spectra of the marine plant residueThSr, matrix UFM and the formulation obtained UFM-ThSr are shown in Figure 3.

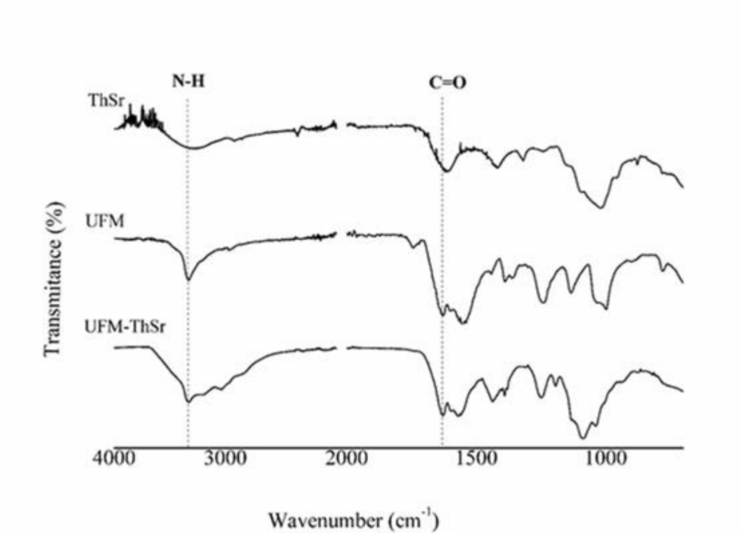


Figure 3:FTIR spectra of the plant residue (ThSr), the matrix (UFM), and UFM-ThSr formulation.

The spectrum of the ThSr residue mixture shows the appearance of multiple peaks due to the high complexity of this plant material. In ThSr, a broad band is observed at 3299 cm^{-1}corresponding to O-H groups of phenolic structures and N-H groups of primary and secondary amides. A small vibration signal at 2924 cm^{-1}indicates the presence of saturated CH_2 groups; while the vibration signal at 1618 cm^{-1} corresponds to the C=O groups of lipids, flavonoids and aminoacids. The signals observed at 1316-1087 cm^{-1}suggest the presence of flavonoids. At 1022 cm^{-1}, the C-OH, C-C, C-O-C bands of polysaccharides are perceived. These signals correspond to the functional groups most commonly located in the main constituent compounds of the cell wall in these species namely the phenolic compounds, proteins and polysaccharides, among others [51].

The resulting UFM spectrum shows an absorption band at 3333 cm^{-1}characteristic of the urea N--H stretching. This characteristic band appears also in UFM-Th Srspectrum (3339 cm^{-1}). Other characteristic peaks presented in UFM and UFM-ThSr were the flexion bands corresponding to the functional group C=O at 1629 cm^{-1} and 1630 cm^{-1}respectively, and NH_2 amide deformation combined with C-N stretch at 1546 cm^{-1} and 1437 cm^{-1}[52-54]. Indeed, interactions between UFM and ThSr could be considered weak as hydrogen bonds or Van der Waals interactions. This could probably help the release of the active ingredients from the prepared matrices.

3.4.2 Scanning Electronic Microscopy (SEM).

Figure 4 shows the results of the morphological study of UFM matrix (a), ThSr residue (b) and UF-ThSr (c) formulation. UFM matrix (a) is characterized by the formation of spherical granules with a tendency to aggregated formation. The sequence of images suggests the microencapsulation of ThSr particle (b) by UFM matrix (a), producing a particle with a larger and irregular surface with tendency to a spherical shape, UFM-ThSr (c). Agglomerates of small, micrometric-size particles of approximately 3 μm can also be observed in UFM-ThSr (c) [50,53,55]. Small particle sizes allow increased surface area for chemical and biological degradation in soil [56]. It is also perceived the presence of cavities, which could contribute to the release of nutrientsinto the environment.

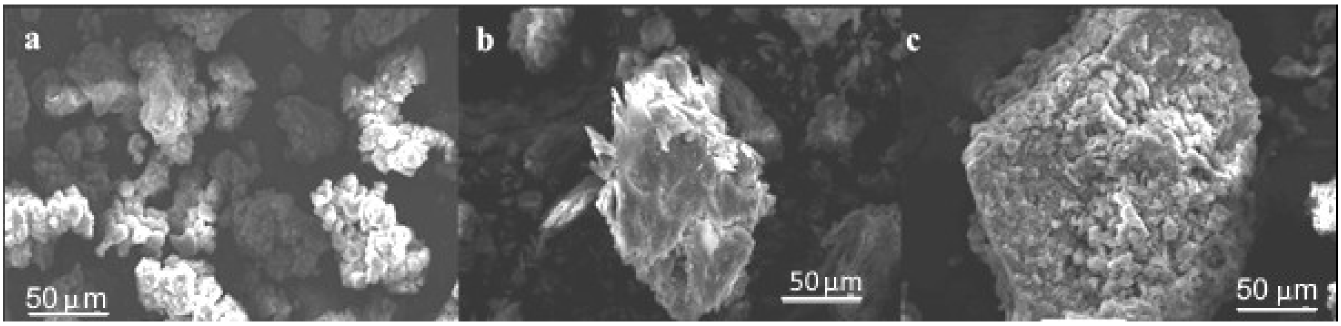


Figure 4: Electron Scanning Microscopy (SEM) of a) UFM b) Thr, and c) UFM-ThSr.

3.5 In vivo studies.

Figure 5 presents the results corresponding to the agronomic parameters evaluated number of total fruits per plant and total yield per hectare, both for the conventional mineral fertilizer CF (Figure 5a), and for the formulation proposed in this study UFM- ThSr (Figure 5b).

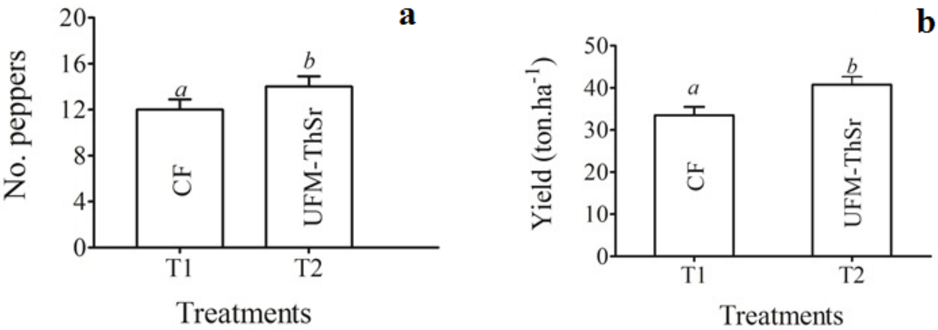


Figure 5: Comparison between the slow release biofertilizer obtained (UFM-ThSr) and CF with respect to: (a) number of peppers per plant and (b) crop yield. Different letters on the bars indicate significant differences between treatments ($p < 0.05$).

Figure 5a shows significant differences ($p < 0.05$) between the application corresponding to UFM-ThSr in the number of peppers per plant (15 ± 0.8), with respect to conventional mineral fertilizer (12 ± 0.9). This resultis favorable, considering that our formulation was administered only once during the vegetative cycle of the crop (30 days), while the CF was applied twice. Like wise, it can be confirmed in Figure 5b that UFM-ThSr formulation presented a higher yield (40.7 t/ha) compared to the CF (33.5 t/ha) ($p < 0.05$). These results are in good agreement witho ther researchers findings, where the brown pepper seeds (*Capsicum annum*) treated with marine macroalga eextracts produced better results in growth parameters (plant height, number of fruits, number of leaves), compared to the use of CF [57, 58].Studies carried out on vegetable crops showed that plants sprayed with extracts from marine plant *Zostera marina* controlled the damage caused by environmental stress, and they also demonstrated a greater activity of tolerance to salinity with respect to control [59].

The main finding of our contribution isthat the crops maintained optimal nutrient availability, through out the cycle with a single application of the obtained formulation (UFM-ThSr), which would allow the reduction of labor costs for its application. UFM-ThSr allows to stimulate the development and growth of crops with nutrients of natural origin. The use of this slow-release formulation prevents harmful processes for both terrestrial and aquatic ecosystems (leaching, denitrification and volatilization). This slow-release formulation constitutes an agroecological solution that allows us to respond to existing environmental problems.

Conclusions

The macro and micronutrient content of the marine plant residues (ThSr) studied gives them a high nutritional value, which confers advantageous uses in the agricultural field. The slow release biofertilizer formulations were obtained from a matrix of UF and marine plant residues by an easy and economical microencapsulation method. All formulated biofertilizers showed a slower macronutrient release behavior compared to CF. The morphology of the UFM-ThSr formulation showed great irregularity and heterogeneity on the surface of the particles. The presence of weak interactions between the matrix (UFM) and the residue studied (ThSr) contributes to the easy release of nutrients. The UFM-ThSr formulation showed greater efficiency in hybrid pepper crops compared to CF, when applied once during the entire vegetative cycle. The use of slow release biofertilizer formulations enriched with marine plant residues is a respectful alternative to reduce adverse effects on ecosystems and the environment. As a future perspective, this product can be suggested for its industrial scaling and its introduction in agriculture in short-cycle crops, in addition to being able to benefit another crop such as rice and its use in gardening.

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