International Journal of Biological Macromolecules 279 (2024) 135202

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: www.elsevier.com/locate/ijbiomac

Review

Polysaccharide-based sustainable hydrogel spheres for controlled release of agricultural inputs

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ARTICLE INFO

Keywords:
Polysaccharide beads
Agrochemicals
Controlled release
Encapsulation
Sustainable agriculture
Hydrogels

ABSTRACT

Producing food in quantity and quality to meet the growing population demand is a challenge for the coming years. In addition to the need to improve the use and efficiency of conventional agricultural inputs, we face climate change and disparity in access to food. In this context, creating innovative, efficient, and ecologically approaches is necessary to transform this global scenario. Several delivery systems are being developed to encapsulate agrochemicals, aiming to improve the controlled release of active ingredients and protect them against environmental biotic and abiotic factors. Among these systems, hydrogel spheres are particularly notable for their ability to be fabricated from biodegradable materials, allowing the encapsulation of molecules, nanomaterials, and even organisms (e.g., bacteria and fungi). This review provides an overview of the latest progress in developing polysaccharide-based hydrogel spheres for agriculture. In addition, we describe methods for preparing hydrogel spheres and discuss the encapsulation and release of agricultural inputs in the field. Finally, we put hydrogel spheres into perspective and seek to highlight some current challenges in the field to spark new inspiration and improve the development of environmentally friendly and cost-effective delivery systems for the agricultural sector.

1. Introduction

Currently, one of the most significant challenges facing the agricultural sector is guaranteeing sustainable food production and meeting the demands of a growing global population while seeking to mitigate environmental impacts [1]. Furthermore, a series of factors, such as i) climate change [2,3], ii) degradation of fertile soils [4], iii) water scarcity [5], and iv) loss of biodiversity [6], are intensifying concerns in this area. In addition, agricultural practices such as deforestation and excessive use of pesticides contribute to increasing environmental problems, harming living beings and human health [7]. All these issues urge humanity to create innovative technologies to improve food production and make agriculture more sustainable worldwide. Among technologies, biomaterials have been improving agro-economy practices - especially natural polysaccharides [8]. They are derived from plants, algae, animals, bacteria, and fungi [9–11], and their structures have advantages over synthetic polymers (with fossil origin) [12] as they are biodegradable and generally require a small amount of toxic reagents for their extraction [13]. Therefore, they are considered eco-friendly and potentially safe materials for environmental applications [14]. In the agricultural sector, they are used in the production of microparticles, nanoparticles, films, and hydrogels [15–18].

The synthesis of micro- and nanoparticles using natural polysaccharides has been focused on controlled-release systems for agrochemicals (pesticides and fertilizers). The nanometer-scale release is a precise approach that offers greater effectiveness in protecting plants [19,20] due to its reduced size and increased surface area. This allows the encapsulated active ingredient within the nanoparticles to interact differently with plants, maximizing the efficacy of conventional treatments while minimizing adverse impacts [21].

For example, lignin [22,23] and chitosan-based nanomaterials [24] can encapsulate agrochemicals and increase their stability against

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https://doi.org/10.1016/j.ijbiomac.2024.135202
Received 30 May 2024; Received in revised form 17 August 2024; Accepted 28 August 2024
Available online 30 August 2024

abiotic and biotic factors in the environment. Furthermore, nanoparticles made up of polysaccharides have been used as seed primers. They provide protective layers to the seeds and prevent diseases/pests [25]. In addition, specific polysaccharides, such as those derived from seaweed (e.g., alginate) or crustaceans (e.g., chitosan), can have biostimulant properties and promote plant growth [26,27] by increasing nutrient absorption [14], regulation of plant hormones, and root growth [28].

In agricultural delivery systems, some platforms may support nanodevices. Hydrogels lead the way since they bring bioavailability in agrochemical delivery into fields, reducing leach rates and toxicity. Hydrogels are porous structures mainly composed of polysaccharides, and they have excellent biocompatibility and biodegradability [12], hydrophilic character, and are three-dimensionally cross-linked. They can absorb and retain immense amounts of water in their interstitial sites [29], improve plant resistance in dry periods, and reduce irrigation needs in arid regions [30]. Hydrogels' polysaccharides can be derived from starch [31], sodium alginate [32], chitosan [33], cellulose [34] and their derivatives (carboxymethylcellulose [35], microcrystalline cellulose [36], cellulose acetate [37]), lignin [38], xylan [39], carrageenan [40], xanthan gum [41], guar gum [42], and pectin [43]. A variety of 3D hydrogel models can be found in the literature: bulk hydrogels, microparticles, spheres, etc [8,44,45].

Hydrogel spheres (also known as beads) made from polysaccharides have gained prominence in the agricultural sector. Their morphologies are like conventional granules but with the benefit of encapsulating various active ingredients and nanoparticles within their structures (Fig. 1). Allowing controlled release of bioactive ingredients [46], reducing the physicochemical degradation and [47] leaching of agrochemicals/nanoparticles into the environment [36]. Furthermore, hydrogel spheres can encapsulate microorganisms to control phytopathogens, protecting them against environmental biotic and abiotic stresses. Thus, they reduce contamination during storage and transport and promote plant growth [48].

A search of the Web of Science (WoS) database from 2013 to 2023 using the descriptors "hydrogel and agriculture and release" yielded 1,043 published scientific articles. Another search using "bead and agriculture and release" descriptors totaled 516 scientific articles published for the same period (Fig. 1-B). However, few systems are manufactured with polysaccharides, indicating a potential area for expansion. Among the works found, polymeric spheres capable of encapsulating conventional agrochemicals (for example, mineral fertilizers, pesticides, and hormones) are the most studied systems, followed by the encapsulation of microorganisms and hybrid systems (classified in this study as spheres containing more than one class of encapsulated compound, such as conventional active ingredients and nanoparticles or microorganisms).

Thus, this review focuses on the latest advances in developing hydrogel spheres consisting of polysaccharides that can encapsulate agrochemicals, nano-enabled agrochemicals, and microorganisms for agricultural purposes. Furthermore, we discuss methods for preparing these hydrogels and their ability to release active ingredients into the environment. Finally, we put into perspective hydrogel spheres for the controlled release of agrochemicals. These systems can contribute to developing eco-friendly and cost-effective solutions to increase agricultural productivity.

2. Exploring methods for producing polysaccharide-based sustainable hydrogel spheres

Producing natural polysaccharides hydrogel has proven promising in sustainable agriculture [13,26]. These materials are abundant in nature, have reduced costs, and have low environmental impact. However, it is essential to understand the process of synthesis of spheres and the materials involved. First, preparation, method, and type of polysaccharide can exhibit different physicochemical properties and enable specific application requirements in the field, such as i) improving the mechanical properties of the system, ii) promoting sustained and/or intelligent release, and iii) increasing environmental compatibility [49]. For example, Qin et al. (2019) successfully produced chitosan-alginate core-shell gel spheres by a dripping method using calcium chloride as a cross-linker. These spheres exhibited a sol-gel transition property responsive to pH stimulation from chitosan and calcium alginate and could release magnetic Fe_3O_4 nanoparticles and fluorescent compounds in an aqueous medium [50].

Nevertheless, most beads are made with cross-linkers aid through physical and chemical interactions [51]. Chemical cross-linkers are recognized for having cross-linkers that form covalent bonds. On the other hand, physical cross-linkers present hydrogen interactions, physical domains, and ionic and hydrophobic interactions [52]. Chemical cross-linkers can be made through the polymerization of monomers or small molecules [53]. Various cross-linkers are used in the construction of hydrogel spheres, such as divinyl sulfone [54], thiourea formaldehyde [55], ethylene glycol dimethacrylic acid (EGDMA) [42], citric acid [56], acrylamide [57], etc. Due to their active groups, these molecules can bind to polymer chains through chemical reactions, including esterification [58] and cross-linking [59]. For example, Knijnenburg et al. (2021) encapsulated zinc oxide nanoparticles in sodium alginate and polyvinyl alcohol (PVA) spheres cross-linked with two ions (Ca^{2+} and Zn^{2+}) through ionotropic gelation. This study observed that hydrogels containing PVA increased water absorption and retention, making them more hydrophilic than those without PVA. Furthermore, the release

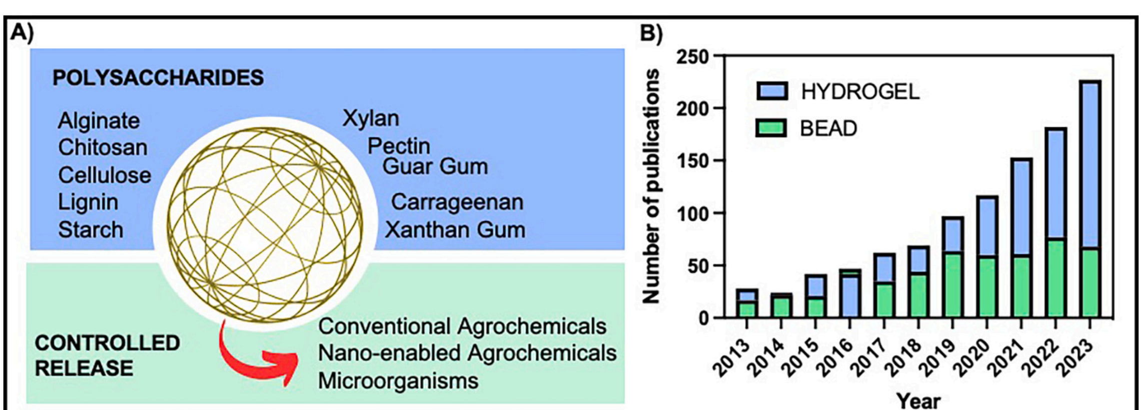

Fig. 1. **A)** Schematic representation of hydrogel spheres considering the main types of polysaccharides and active ingredients that can be used for the agricultural sector; **B)** Number of papers published using descriptors "hydrogel and agriculture and release" (blue bars); "bead and agriculture and release" (green bars) in the ISI Web of Knowledge database from 2013 to 2023.

kinetics were found to be dependent on the cross-linker used, as the spheres cross-linked with Zn released the ion quickly, while those cross-linked with Ca were slower [60].

Inappropriate use of cross-linking agents can cause changes in the physicochemical properties of polysaccharides, altering their surface area, particle size, volume, and pore dimensions and affecting their thermal degradation and swelling of the polymer [61]. For example, using concentrations of cross-linker that are higher than necessary can result in denser and more rigid three-dimensional networks. This can impede the mobility of molecular chains, reducing the interstices between the liquid molecules in the network [62]. On the other hand, epichlorohydrin, a cross-linking agent commonly used in polysaccharides, can control the hydrogel's swelling and thermal stability. That is, as the concentration of this molecule increases, the swelling capacity decreases, and the material's thermal stability improves [40]. Therefore, the concentration of cross-linkers is fundamental, and their use depends on the type of biopolymer and the desired properties of the material.

Besides cross-linkers, parameters such as temperature and pH can interfere with the synthesis of hydrogel spheres. For example, Cai and Zhang (2006) showed an interaction between cellulose and NaOH in an aqueous urea solution (pre-cooled below −10 °C) where they rapidly dissolved cellulose at room temperature. Furthermore, their results showed cellulose gelation when dropped in the 59.4 °C–30.5 °C range and irreversible gel behavior at temperatures above 30 °C or below −3 °C [63]. Therefore, changing temperature can alter the viscosity of polysaccharide solutions since molecular interactions and movement of polymer chains are affected by changes in the thermal energy of the solution [64]. Under higher temperature conditions, for example, greater sphericity of the material [65] and an increase in swelling capacity can be achieved [66]. Additionally, temperature is closely linked to the active ingredient release processes. At lower temperatures, around 4 °C, reducing the diffusion of the active ingredient to the external environment is possible since structural changes may occur in the spheres, making them more compact or altering their porosity [67].

Furthermore, changes in pH values can influence the mechanical properties, such as tenacity and hardness of hydrogels, due to their interactions between polymer chains that can form cross-links, increasing the rigidity and resistance of the gel [68]. Furthermore, when the sphere construction process is used to encapsulate cells or microorganisms, the pH during their formation can impact the viability and performance of the encapsulated organisms [69]. Thus, pH optimization is fundamental in designing and manufacturing these materials for various applications.

On the other hand, another factor that can influence the preparation of hydrogel spheres is the mixture of polysaccharides with inorganic substances, including metallic oxides and silica, in their composition [8]. This association can provide unique and combined properties between two or more systems, such as excellent structural stability, mechanical resistance, and capacity for controlled release of active substances. It can also result in structures with high porosity, low density, and resistance to extreme temperatures [70]. For example, Eddara et al. (2022) manufactured chitosan and kaolinite clay spheres by dip-immersion for controlled release of NPK fertilizers. They observed that the inclusion of clay affected the mechanical properties of the system, resulting in better physical resistance, increased cation exchange capacity with the soil, and delayed degradation and release of the active ingredient compared to those containing only chitosan [71]. Furthermore, incorporating inorganic nanoparticles uniformly distributed in the matrix of polysaccharide spheres is another strategy used to increase the hydrogel's resistance in acidic or alkaline media and improve its thermal stability [72].

3. Hydrogel spheres as delivery systems

The development of intelligent systems for the controlled release of agrochemicals and microorganisms that are biodegradable, low-cost, and scalable has attracted the attention of the agricultural sector. In this context, hydrogel spheres composed of polysaccharides can improve the effectiveness of agrochemicals, reducing the number of applications required and decreasing the irrigation frequency since these spheres are superabsorbent and can protect active ingredients. However, release mechanisms in complex matrices (such as soils and tributaries) have yet to be fully elucidated. The primary rationale is based exclusively on the swelling caused by osmosis in the polymeric network. The water absorption increases pressure, swells the hydrogel, and stretches the polymeric network as the pores expand, allowing permeabilization to the environment [73]. A possible mechanism for the release of agrochemicals/microorganisms in hydrogel spheres in the soil can be interpreted as shown in Fig. 2A, followed by the steps: 1) it begins with the expansion process (swelling), which aims to facilitate the diffusion of the encapsulated compound; 2) then, there is a migration of free water towards the interior of the coating through the pores, contributing to triggering the release; 3) subsequently, the polymer itself gradually disintegrates, a process driven by environmental microorganisms during the decomposition phase, thus, accelerating the release process [74]. However, it is worth noting that in the case of encapsulation of microorganisms or nano-enabled agrochemicals, other factors may influence this release model.

The release rates of (nano-)agrochemicals/microorganisms can also be controlled by changing the thickness and total content of the encapsulated active ingredient [57,75]. Furthermore, aspects such as crystallinity, material composition, surface charge, type and concentration of active ingredient, particle size, hydrophilic-hydrophobic interactions, porosity, and cross-linking are related to the spheres' degradation (and release) mechanisms [51]. Therefore, surface morphology is extremely important since spheres with well-defined porous structures absorb more water, facilitating compounds' degradation and release rate. Thus, mixing different materials enables the design of new surface roughness, pores size, and release mechanisms of active ingredients [76]. For example, sodium alginate is the polysaccharide most used in developing these hydrogel spheres as it meets the requirements such as good biocompatibility, biodegradability, and non-toxicity. However, when the spheres are made purely of alginate, they have low mechanical resistance, which limits their applications [60].

Changing spheres' structures and understanding physical-chemical behaviors (alongside resistance, surface, thickness, and pore size) have been challenging [77]. For example, Li et al. (2016) produced a series of alginate- and kaolin-based beads with surface modification with polyethyleneimine (PEI) and polysaccharides fillers: cellulose powder, cellulose nanocrystals, starch, and xylan (Fig. 2 B1, B2 and B3). Their results indicated that the addition of an inorganic clay such as kaolin improved the spheres' mechanical resistance, the surface modification was directly proportional to the control of phenylacetic acid (a plant growth regulator) release rate, and cellulose nanocrystals caused rougher surfaces [39].

Another way to modify beads is by incorporating a polymer derivative (a polymer with chemical modifications), e.g., carboxymethyl cellulose (CMC) - Fig. 2-B4 - is known to improve water mobility and porosity of the spheres [78]. As previously mentioned, physicochemical proprieties may also differ with cross-linking molecules. Perez et al. (2016) examined spheres produced from a mixture of starch and chitosan using the dripping technique in an aqueous solution of sodium tripolyphosphate (TPP) as an ionotropic cross-linking agent (Fig. 2-B5). They observed that the starch content and cross-linking time affected the characteristics of the spheres, influencing the swelling behavior and fertilizer release capacity [79]. Furthermore, beads such as those derived from lignin, a polyphenolic material, can be degraded by bacteria and fungi, enabling its use in constructing microorganism-responsive beads. Lignin beads can also improve the slow-release behavior of fertilizers and the effectiveness of pesticides such as atrazine [80,81]. Beads containing only alginate or chitosan may exhibit a slow degradation rate by microorganisms; however, this rate may vary

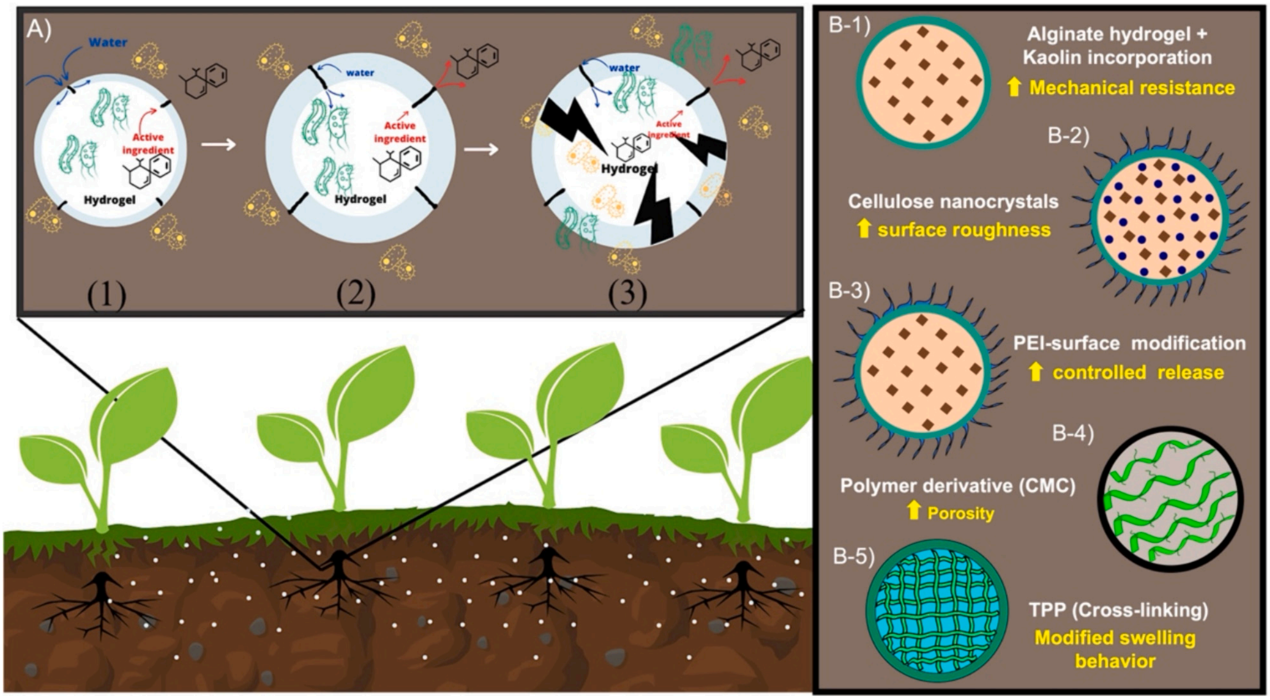

Fig. 2. A) Scheme of the controlled release mechanism of polysaccharide spheres: 1-Water from the environment penetrates the structure of the sphere through the pores, causing its expansion; 2-Migration of free water into the sphere causes the diffusion of the active ingredient into the environment through the pores of the hydrogel; 3-Microorganisms promote residual degradation of insoluble active ingredients. B) Examples of different hydrogel spheres and their effects when adding other materials to the system (B1 and B2), applying a new coating (B3), or mixing with different polysaccharides (B4 and B5). Parts of the figure were created using canva.com.

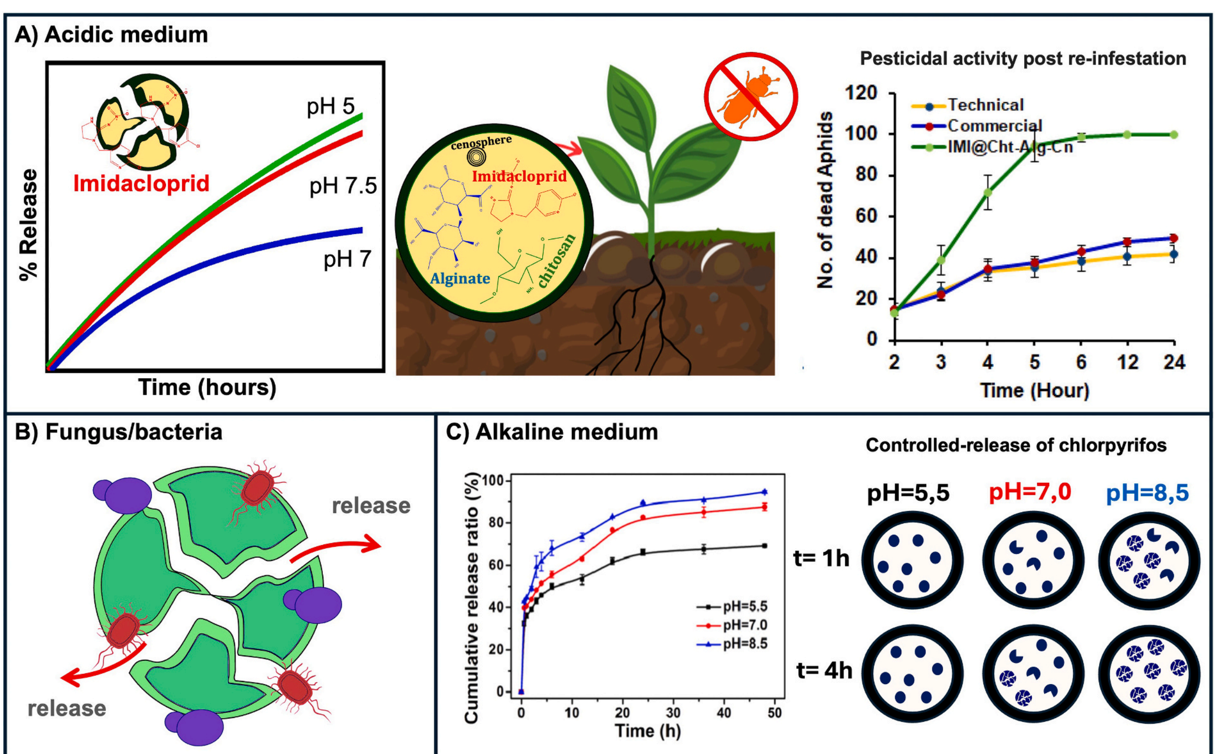

Fig. 3. Examples of responsive release hydrogel spheres: A) pH-responsive release of imidacloprid from hydrogel spheres and their pesticidal activity following re-infestation of aphids after 48 h, B) Fungus-bacteria responsive release hydrogel, and C) pH-responsive chlorpyrifos hydrogel sphere and their cumulative release rate in different pH. Reproduced with permission from Ref. [83,86] Copyright (2022, 2018), Elsevier. Parts of the image were created using canva.com.

due to their specific chemical structures and environmental conditions [33,80].

3.1. Encapsulation of conventional agrochemicals in hydrogel spheres

The encapsulation of conventional agricultural inputs such as pesticides and fertilizers [7,82] in polysaccharide matrix hydrogel spheres opens new possibilities for the sustainable management of agricultural inputs in a more efficient and ecologically conscious pathway by reducing the degradation of active ingredients against biotic and abiotic factors and improving their availability to plants.

A study by Singh et al. (2022) on encapsulating the insecticide imidacloprid in hydrogel spheres composed of chitosan, alginate, and cenosphere revealed that insecticidal activity was achieved without affecting the host plant in the long term. The leaching analysis indicated that the loss of the active ingredient was twice as slow, at only 12 %, compared to the commercial formulation. Furthermore, insecticidal efficacy reached 100 % against *Aphis crassivora* (cowpea aphid) over 48 h, demonstrating superior performance compared to the conventional formulation. The authors also observed pH responsiveness in the beads (Fig. 3A) [83]. Parallel to this study, hybrid spheres of polysaccharides and clay showed great potential for water retention and prolonged release of up to 60 times greater than non-encapsulated active ingredients [84]. Yan et al. (2013) also developed a hybrid system of alginate, chitosan, and bentonite prepared by extrusion in a calcium chloride solution. The inclusion of bentonite demonstrated the potential to improve the particles' sphericity, causing the insecticide acetamiprid's loading rate and encapsulation efficiency to increase from 36.36 % to 63.01 %. While the sphere containing only chitosan and sodium alginate increased from 36.36 % to 54.29 %, the synergism between the mixture also improved the release performance [85].

Furthermore, Li et al. (2012) produced hydrogel spheres composed of carboxymethyl chitosan and bentonite to encapsulate atrazine (an herbicide) and imidacloprid (an insecticide). The release study showed that the time required to release 50 % of the active ingredients (t_{50}) was extended to 572 h for atrazine and 24 h for imidacloprid. The difference in release behavior between the two herbicides is related to the active ingredient's hydrophobicity and water solubility. In addition, leaching studies showed that the amount of pesticide available decreased due to the sorption promoted by bentonite [87]. Also, the construction of hydrogel spheres developed by Liu and colleagues (2021) for the controlled release of clothianidin, using tannic acid/Fe(III) as a coating and sodium alginate as a matrix, showed long-lasting effectiveness in managing the bean aphid, increasing the absorption and bioconcentration capacity of clothianidin in plants [88].

Hydrogels that respond to external parameters are gaining attention for releasing bioactive ingredients, as biodegradable beads can degrade in contact of bacteria and fungus of soil (Fig. 3B) [80]. Also, Xiang et al. (2018) developed a pH-responsive controlled-release nanosystem composed of chlorpyrifos, polydopamine, attapulgite, and calcium alginate. The results indicated that the spheres tended to collapse in an alkaline environment and promoted the release of chlorpyrifos, demonstrating their effectiveness in combating larvae (grubs) (Fig. 3C). Furthermore, the system protected the active ingredient from ultraviolet light, which is considered promising for extending the pesticide's duration in the field [86].

On the other hand, hydrogel spheres can entrap and control the release of fertilizers, such as Nitrogen, Phosphorus, and Potassium (NPK), showing greater efficiency than conventional fertilizers due to the slower release of these nutrients [89,90]. For example, Chen et al. (2023) produced a potassium-based fertilizer encapsulated in a starch-alginate matrix. They observed that the ability to control the release of the nutrient was associated with the concentration of polysaccharides used in preparing the formulation. Higher concentrations of sodium alginate, combined with lower concentrations of potassium chloride, achieved good encapsulation efficiency, decreased swelling, reduced potassium release, and a 25 % increase in the spheres' biodegradation rate [91]. Therefore, research and development in this area can potentially improve the use of agrochemicals. Technological advancement meets the efficiency requirements of modern agriculture and the growing demand for sustainable agricultural practices that involve circular economy precepts. Table 1 summarizes other examples of agrochemicals encapsulated in hydrogel spheres for agriculture.

3.2. Encapsulation of microorganisms in hydrogel spheres

Microorganisms play an important role in promoting plant growth, protecting against pathogens and pests, improving soil quality, and increasing agricultural productivity [103]. Microorganisms have multiple mechanisms of action in plant growth, such as the production and secretion of phytohormones such as indole-3-acetic acid (IAA), cytokinins, gibberellins, and ethylene; plant growth regulators (abscisic acid, nitric oxide, and polyamines such as spermidine, spermine); increased nutrient availability, phosphate solubilization, nitrate reductase activity, and N use efficiency; biocontrol of phytopathogens and diseases; protection of plants against saline stress and toxic elements in the soil; in addition to biological nitrogen fixation. In this way, bacteria, fungi, and other beneficial microorganisms can be used to enhance plant development [13,104] and agricultural productivity [105,106]. Therefore, the interest in encapsulating microorganisms in polymeric carrier systems has increased [104] since many of these organisms can suffer from abiotic environmental factors, and encapsulation can protect them, making them more available over time. Thus, the encapsulation of microorganisms in polysaccharide spheres is of great value. Being hydrophilic, they can improve the moisture retention capacity of the inoculants, which is crucial for the survival and growth of microorganisms in the environment [47] (Fig. 4).

Plant growth-promoting and nitrogen-fixing rhizobacteria in soil are efficient candidates for field application. They can potentially increase crop productivity, suppress plant diseases, and act as biofertilizers [107]. For example, Lima-Tenorio and colleagues (2023) conducted a study using a mixture of cationic starch polysaccharide and chitosan to produce a biofertilizer. In this way, AbV5 and AbV6 strains of *Azospirillum brasilense* were encapsulated inside a double sphere by a swelling diffusion method followed by desiccation. The spheres were obtained using the dripping technique and cross-linked with sodium tripolyphosphate. The results showed that the treated plants maintained the viability of *A. brasilense* for at least 60 days and demonstrated efficiency in promoting corn growth [108]. Also, Chen et al. (2013) used this method to encapsulate *Bacillus cereus* (strain C1L) and maintained 42 % of its viability. They used 18.3 % maltodextrin and 12.5 % gum arabic as coating materials to act as a biofungicide, and this system effectively protects encapsulated bacteria and inhibits *Cochliobolus heterostrophus* [109].

On the other hand, fungal entomopathogenic organisms can be a promising alternative to synthetic insecticides for the biocontrol of pests and insects. For example, encapsulation in calcium alginate and starch spheres was used to encapsulate the fungus *Metarhizium brunneum* (BIPESCO5), considered a beneficial organism for pest control, capable of promoting endophytism in tomato plants. Thus, mycelium encapsulation increased drying survival by 31.5 %. The co-encapsulated starch was degraded by 24.8 % after 21 days and served as a source of nutrients for its growth in soil. When applied to soil, encapsulation significantly increased endophytism by 3.8 to 7.0 times compared to plants treated with unformulated fungal biomass [110]. In another study, hydrogel spheres were produced by the ionic gelation method in a sodium alginate matrix modified with different polymers to encapsulate the *Trichoderma* sp. fungus (a potential biological control agent) to evaluate the viability of conidia during encapsulation. The results revealed good compatibility with Trichoderma, as formulations stored after 14 months showed concentrations of viable cells above 106 CFU/g [111]. Also, Muskat et al. (2022) encapsulated the fungus *Entomophthorales Pandora*

Table 1
Examples of conventional agrochemicals encapsulated in hydrogel spheres and their main results.

Sphere type	Agrochemical	Findings	Ref
Alginate/Bentonite	Emamectin benzoate	Effective in controlling *Spodoptera frugiperda* in corn plants. Bentonite content increased and the release rate decreased.	[92]
Starch/Chitosan/Calcium Alginate	Spirotetramat	Controlled release and slow degradation rate. Improved insecticide efficacy.	[93]
Sodium alginate/Chitosan	Chlorantraniliprole	Controlled release of the insecticide and better efficiency in controlling *Chilo suppressalis* and *Sesamia inferens*.	[94]
Starch/Sodium Alginate/Natural Rubber	2,4-dichlorophenoxy	The system improved bioavailability and prolonged herbicide release for 700 h.	[95]
Carboxymethyl chitosan	Prothioconazole	The system showed pH-responsive release for the insecticide, good fungicidal capacity against *Gaeumannomyces graminis* var. *tritic,* and decreased dosage of insecticide.	[96]
Sodium alginate/PNIPAM	Glyphosate	The system showed multi-responsive release for the herbicide.	[97]
Cellulose	Zinc sulfate	Capacity for nutrient release and absorption by plant roots.	[98]
Sodium Alginate/Lignin	Ferric chloride	Sustained iron release behavior and degradation rate of 55.6 % after 50 days of exposure in the soil.	[99]
Alginate/Lignin	Potassium nitrate/Potassium phosphate	Prolonged release of fertilizer over 25 days. Variations in alginate/lignin concentrations directly affected the a.i. release.	[100]
Sodium alginate	Ammonium nitrate/Potassium chloride	The system decreased the nutrient release rate compared to pure salts.	[101]
Sodium alginate/carboxymethylcellulose	Cu^{2+} ions	Slow release of micronutrients, good bioavailability, and lower fertilizer application rates.	[102]

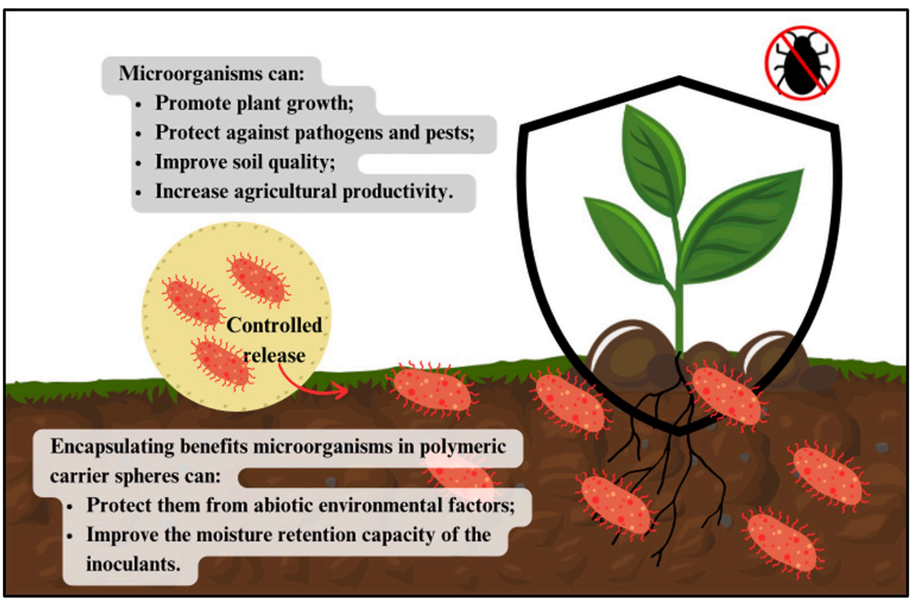

Fig. 4. Action and benefits of controlled release of microorganisms encapsulated in polymeric carrier systems into the soil. Image was created using canva.com.

sp. (ARSEF 13372) to develop a biopesticide in the form of spheres using the extrusion method. Thus, various combinations of sodium alginate with starch, chitin, and skimmed milk powder were used to encapsulate the fungal conidia. Hence, skimmed milk increased the number of fungal conidia by 2.95 times and released a significantly greater number of conidia from the spheres than the other combinations. Furthermore, a higher mortality rate of the formulation was observed for summer apple psyllid pests, e.g., about 48 % for *Cacopsylla picta* and 75 % for *Cacopsylla pyri* [112].

It is worth highlighting that according to Wu et al. (2012), when microorganisms are incorporated into a hybrid matrix composed of clays and natural polymers, the clay can increase the cellular stability of the encapsulated microorganisms, forming a protective layer against adverse conditions, such as changes in temperature, pH among others, improving the overall stability and survival rate of encapsulated cells [113]. Furthermore, clays in polymeric spheres improve interaction with microorganisms present in the environment [114,115]. Also, spheres manufactured from chitosan/carbon black nanopowders can adsorb phosphate. When in contact with microorganisms, these spheres decompose, releasing primary nutrients (nitrogen, phosphorus, and potassium) [116,117]. Therefore, encapsulation of microorganisms is a promising technique that continues to evolve and offers innovative solutions to various challenges across different industries. In general, it can be difficult to study the effect of microorganisms on polymeric and hybrid polysaccharide spheres due to the complexity of interactions between microorganisms and the physicochemical properties of the spheres, which can influence the growth and activity of microorganisms [118]. Therefore, as research and development in this area progresses, the application of encapsulated microorganisms in agriculture is expected to become more effective, playing an increasingly important role in promoting sustainability and improving agricultural practices worldwide. Table 2 presents other examples of microorganisms encapsulated in hydrogel spheres and the main results obtained from these studies.

3.3. *Encapsulation of hybrid systems in hydrogel spheres*

With advances in the production of hydrogel spheres, the ability to encapsulate multiple active ingredients within their structure arises, creating hybrid systems. These systems combine different

Table 2
Examples of microorganisms encapsulated in hydrogel spheres and their main results.

Sphere type	Microorganisms	Findings	Ref
Chitosan/Starch	*Azospirillum brasilense/ Pseudomonas fluorescens*	Immobilization of bacteria in hydrogel spheres benefits bacterial survival rates. Promotion of root growth in corn plants.	[119]
Alginate-montmorillonite/Alginate-halloysite	*Pseudomonas fluorescens/ Azosprillum brasilense*	Slow release of plant growth-promoting bacteria after 15 days of incubation and effectiveness on the growth of wheat plants.	[120]
Sodium alginate	*Enterobacter hormaeche*	Significantly higher okra growth and yield were observed after 60 days. Soil quality improved, with a yield increase of up to 75.6 %.	[121]
Gelatin alginate	*Enterobacter* sp. ITCB-09	The bacterial strain exhibited the ability to solubilize inorganic phosphate (865.98 μg/mL). Positive effect on *Capsicum chinense* Jacq. seedling growth.	[122]
Sodium alginate/Calcium chloride	*Trichoderma harzianum*	Increased levels of denitrifying bacteria compared to control. Enhanced chitinolytic and cellulosic activities, resulting in effective control of *S. sclerotiorum*.	[123]
Gum Arabic/Maltodextrin	*Bacillus subtilis B99-2*	The survival rate was 87.53 % after 540 days of storage. Effective biocontrol reached 79.91 % against *Rhizoctonia* tomato rot under field conditions.	[124]
Alginate/Carboxymethylcellulose/ Pectin	*Heterorhabditis* sp.	The alginate spheres demonstrated nematode retention capacity.	[125]
Starch/Chitosan	*Azospirillum brasilense/ Pseudomonas fluorescens*	Controlled release of bacteria into water and soil.	[126]

interconnected components within the same matrix, enabling the sequential release of multiple active ingredients over time [127]. For example, nutrients can be encapsulated with components that reduce soil acidity, contributing to a better productivity culture, or nanoparticles associated with microorganisms can be used [128]. For example, spheres made of slow-release sodium alginate that enable the release of insecticides and fertilizers (organic and inorganic) in a single application were developed by Joshi et al. (2020) using the microorganism *Bacillus thuringiensis* as a biopesticide and nitrogen, phosphorus, and potassium as fertilizers. The results showed different release patterns between the encapsulated active ingredients, with KNO_3 and K_2HPO_4 showing a monophasic prolonged release pattern. In contrast, nitrogen showed a lower release rate during the same 24-h of study. Regarding the effectiveness of this biopesticide against *Heliothis virescens* larvae, a 35 % survival rate was reported, while the control achieved 72.5 % after 120 h of exposure [129].

The association of different active ingredients in hydrogel spheres was also observed by Ma et al. (2023), who prepared double-layer spheres for the controlled release of various nitrogen, selenium, and copper-based fertilizers. Urea was encapsulated as the core of the fertilizer, and copper ions were present in the outer shell of the hydrogel. In addition, mesoporous silica nanoparticles loaded with sodium selenate were encapsulated in the hydrogel network. In this study, the release time of nutrients from the sphere reached approximately 42 days, as the outer layer of the hydrogel increased the diffusion distance of nutrients, thereby prolonging the release time. However, the slow release of Cu^{+2} showed an antifungal effect, improving cherry radish's productivity and nutritional value (*R. sativus*) [127].

In the meantime, the encapsulation of nanoparticles associated with nutrients, biopesticides, or even microorganisms in hydrogel spheres has also been the target of investigation, as nanoparticles may behave differently than conventional active ingredients. For instance, Ekanayake et al. (2021) synthesized a dual-functional alginate hydrogel containing ZnO and CuO nanoparticles. They observed that the loosely held ions in the hydrogel were released before the cross-linking ions in the polymer chains (Fig. 5-**A**) [130]. Also, Pour et al. (2022) encapsulated *Bacillus velezensis* in an alginate gum polymer hydrogel enriched with TiO_2 and SiO_2 nanoparticles and observed that the bacteria remained viable and were released from the carriers for >50 days (Fig. 5-**B**) [131]. In addition, Panichikkal et al. (2021) produced hybrid spheres composed of alginate, salicylic acid, zinc oxide nanoparticles (ZnO NPs), and *Pseudomonas* sp. DN18. This system showed antifungal activity against *Sclerotium rolfsii*. In addition, it revealed that plant growth and biocontrol properties were superior to those of *Pseudomonas*

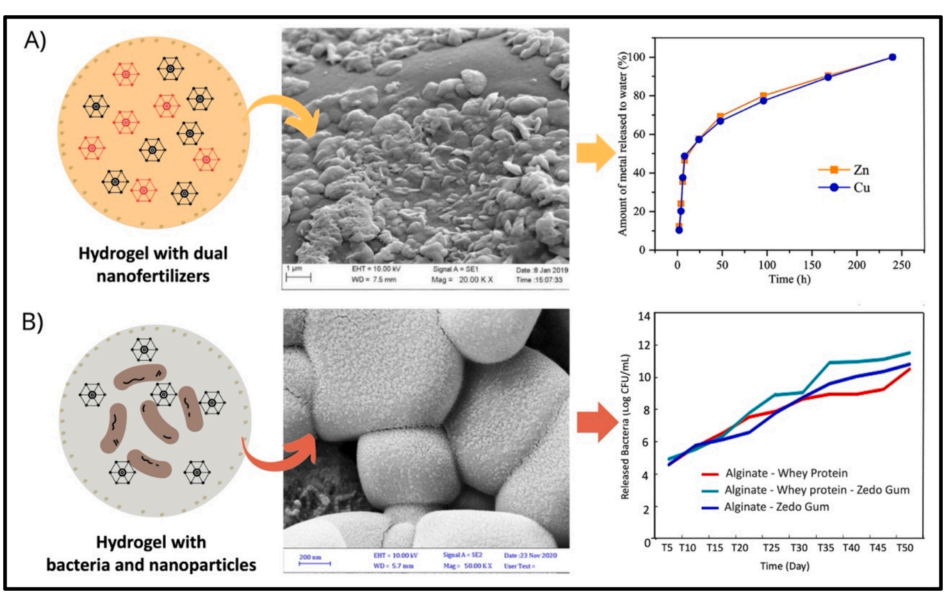

Fig. 5. Examples of encapsulation of hybrid systems in hydrogel spheres. A) Hydrogel spheres with dual-functional nanofertilizers embedding ZnO and CuO nanoparticles. Reproduced with permission from Ref. [130] Copyright (2021), American Chemical Society. B) Hydrogel encapsulated with *Bacillus velezensis* and TiO_2 and SiO_2 nanoparticles. Reproduced with permission from Ref. [131] Copyright (2022), MDPI. Parts of the image were created using canva.com.

sp. DN18 in trials using rice (*Oryza sativa*) seedlings [128].

Furthermore, hydrogel spheres can be engineered according to their application by mixing materials to modulate active ingredients' release effect or promote compatibility with specific microorganisms. For example, Humbert et al. (2017) described the synthesis of hydrogel spheres from calcium alginate chloride to encapsulate amyloglucosidase and *Saccharomyces cerevisiae* and to assist in releasing CO_2 [132]. The production of CO_2 from yeast acted as a biocontrol agent against pests, and it was even possible to encapsulate compounds with insecticidal properties that could interact with the encapsulated microorganisms [133,134]. Another study evaluated the release of CO_2 from synergistic interactions between a *Beauveria bassiana* fungus with *Saccharomyces cerevisiae* and corn starch, prolonging and increasing the release of CO_2 [135].

Therefore, developing new sustainable hybrid systems with intelligent release capacity is crucial to enable agricultural productivity [1]. Thus, with hydrogel spheres, it is possible to encapsulate and control the release of different nanofertilizers. For instance, Vincekovic et al. (2016) produced a chitosan/alginate-based hydrogel sphere, co-encapsulating with the microorganism *Trichoderma viride* and the micronutrient copper, offering multiple effects in the field. Their results revealed that release can be controlled by both the size of the spheres and by incorporating the microorganism into their matrix [136]. Furthermore, such systems can potentially present a slow release when the nanoparticles are encapsulated within them.

4. Concluding remarks and future perspectives

The evolution of technology and global challenges are constantly changing in the agricultural sector. It is crucial to anticipate and understand the trends that will guide us to achieve safe and efficient systems in the coming years. Developing intelligent systems for the controlled release of agrochemicals is already a reality [137,138], and nanotechnology plays a critical role in improving these systems [139]. However, when moving towards the use of beneficial microorganisms in plants, encapsulation in nanoparticulated systems is not as suitable due to their size, as many of these microorganisms have a larger structural organization than nanometric systems. In addition, such organisms are in constant metabolic activity, carrying out a series of biological processes, such as cell replication and cell division, among others [113,121].

Furthermore, microorganisms are highly susceptible to dehydration and quickly lose viability [69,108]. In this way, developing new intelligent materials, such as hybrid spheres made of polysaccharides, makes it possible to create structures resistant to adverse climatic conditions to encapsulate microorganisms and increase their viability in the field. These structures can also provide food for survival and multiplication, allowing the encapsulation of conventional agrochemicals and nanoparticles. Therefore, hydrogel beads have the potential to significantly improve the use of microorganisms and other active ingredients in traditional agriculture, promoting more sustainable agricultural practices and boosting responsible food production on the planet. Numerous patents have been issued on this topic (e.g., US 10,865,160 B2; US 7,422,737 B1). However, there are still challenges to be overcome for the full implementation of this technology, such as:

- Some hydrogels, such as spheres made solely of alginate, can be difficult to degrade in soil, significantly delaying the release of the active ingredient. To overcome this, it is necessary to develop more complex systems, such as hydrogels combined with clays, organic matter, or other biodegradable polymers.
- The size of the hydrogel spheres limits their application mainly to soil, as foliar application remains inefficient. Their size prevents internalization or adherence to the leaf. However, strategies can be developed to modify the size and surface of the spheres by using coatings that enhance adhesion to the leaf surfaces.
- There is a need for in-depth studies on the release mechanisms of these hybrid systems, especially for bacteria and hybrid systems under real environmental conditions. Furthermore, responsive polysaccharides should be further explored to control the release of active ingredients. For example, chitosan can generate a system responsive to changes in pH [83], while xanthan gum can create a system responsive to temperature due to its rheological changes, such as changes in viscosity and stability [140].
- The production cost of hydrogel spheres can be high, especially when considering large-scale agricultural applications. Therefore, cheap and innovative methods of manufacturing hybrid hydrogel bead systems must be improved. For example, Jiang et al. (2023) created a rapid process of producing spheres using the Pickering emulsion method. In this method, droplets surrounded by layers of air and water are formed by an air jet passing through a small reservoir containing a liquid layer composed of a suspension of nanoparticles and biopolymer, allowing the generation of up to 300 spheres per second [141]. Furthermore, the spray drying technique is also used to produce these systems on a larger scale [142]. However, it has limitations related to the stability of the complex precursor solution/dispersion during the atomization process, high energy consumption, etc. [143].
- There is a need for a better understanding of the impact of these systems on the environment and human health, particularly when involve multiple active ingredients or nanomaterials. The effects of these hydrogel spheres should also be based on the timing of application and different environmental conditions. This understanding is crucial for supporting regulatory processes and ensuring acceptance by producers and the public in the future.

In addition, this study suggests new strategies for developing formulations based on hydrogel spheres. The main future perspectives include:

- Investigate how different combinations of polysaccharides and microorganism agents can further improve the efficiency and sustainability of hydrogels, adapting them to a broader range of adverse environmental conditions and other crops.
- Explore the use of nanomaterials with improved properties, such as greater controlled release capacity and responses to specific environmental stimuli (pH, temperature, humidity, etc.).
- Promote the development of materials integrated with precision agriculture technologies for more efficient and localized administration of agricultural inputs, reducing waste and maximizing yields.
- Conduct large-scale field trials to evaluate the effectiveness of these materials in various agricultural conditions and climates, providing real data on their performance and economic and environmental benefits.
- Conduct environmental impact studies and life cycle analyses to quantify the benefits and potential drawbacks of widespread adoption of hydrogels in agriculture, helping to develop guidelines for their sustainable use.
- Explore the encapsulation of new types of active ingredients, such as biofertilizers and beneficial microorganisms with pest biocontrol capabilities, to broaden the reach of the technology and promote even greener agriculture.

Therefore, developing and implementing new strategies for the controlled release of agricultural inputs is essential to mitigate environmental impacts and improve food production. In this way, we hope that innovation research will continue to explore new ways to harness the potential of these hydrogel spheres for the agricultural sector, always aiming to contribute to more sustainable and efficient farming practices.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

CRediT authorship contribution statement

Débora R. Antunes: Writing – review & editing, Writing – original draft. **Mariana M.L.H. Forini:** Writing – review & editing, Writing – original draft. **Érica R. Biscalchim:** Writing – review & editing, Writing – original draft. **Pedro H.C. Lima:** Writing – review & editing, Writing – original draft, Conceptualization. **Luiz A.F. Cavalcante:** Writing – review & editing, Writing – original draft. **Marcelo C.M. Teixeira Filho:** Writing – review & editing, Writing – original draft. **Durgesh K. Tripathi:** Writing – review & editing. **Javier Pitti Caballero:** Writing – review & editing, Writing – original draft. **Renato Grillo:** Writing – review & editing, Writing – original draft, Supervision, Funding acquisition, 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

The datasets used and/or analyzed during the current paper are available from the corresponding author on reasonable request.

Acknowledgment

São Paulo Research Foundation (FAPESP, grant number: #2022/03219-2), National Council for Scientific and Technological Development (CNPQ, #440214/2021-1), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, Finance Code 001) and Secretaría Nacional de Ciencia, Tecnología e innovación (SENACYT, Proyecto: FIED21-036). M.M.L.H.F. thanks FAPESP for the fellowship (#2023/09217-4).

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