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# Advances in controlled release systems for sustainable crop production: A review of nano-, micro-, and macro-formulations

Stefano Di Rago [b], Francesco Morandi [b], Fabio Pizzetti [*], Filippo Rossi [**]

*Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133, Milan, Italy*

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ABSTRACT

The high necessity to develop novel and optimized technologies for crop production is very high due to the exponential growth in term of world population of the last years. In this field a novel use of fertilizers and pesticides can ameliorate the life conditions around the world due to the higher productivity with lower losses and consequent less environmental problems related to pollution. To address these challenges a very promising solution is constituted by devices able to control and sustain the release of fertilizers and pesticide optimizing their efficacy preserving the environment. In the last decade a lot of efforts, in terms of research, were dedicated to the development of smart devices that can address those issues maintaining also low costs and easy production processes. In this review we will point the attention on devices that can be used as slow release systems for fertilizers and/or pesticides. In details strong consideration will be devoted to their formulation to increase the knowledge on the high number of possibilities behind these novel and smart devices.

## 1. Introduction

Controlled release systems appear as relative novel applications in the agricultural sector, and they are exceptionally sought after for their ability to deliver fertilizers and pesticides over a prolonged period of time. Nowadays, it is of foremost importance to optimize fertilizers and pesticides usage in order to achieve the best performances in terms of yield, soil composition, production's costs and sustainability.[1,2] A prove of that is represented by the high importance that this field has in the research community. Indeed the number of publications about slow release systems (SRS) has increased exponentially over the years (Fig. 1),[3] underling the growing interest for this topic and its role as a possible solution to some major problems. In the first place, the deployment of long-term slow-release systems enables farmers and industries to reduce operating hours and reduce production costs as a consequence.[4–7] Moreover, the slow release is essential to permit the plant to absorb the fertilizers gradually, maintaining good yield performances while improving the production's quality and the soil microbial diversity, as it was shown in a study on litchi production[8] and in a two-year field experiment on apple trees.[9] From an economical point of view, slow release solution represents a new frontier to reduce costs while increasing the yield of the production.[10,11] The growing interest for fertilizers and pesticides long-term release led to a huge variety of new controlled release systems used in different applications. In rice and oil-seed rape crops, these systems promoted a sharp increase in the yields by 23–42 % and 106–187 % respectively.[12] Lan and coworkers[13] showed how the controlled release systems had an effect on the yield by increasing the amount of grain per spike and the weight in an experiment on grain cultivation. Additionally, they demonstrated that leaves lifespan was extended thanks to a continuous supply of nutrients to the plants. This result underlines the great impact of SRS on agricultural application, also considering that systems loaded with a dose of fertilizer performed similarly to the same fertilizer used in a two-fold dose.[12] In terms of sustainability, these solutions are totally degradable and do not have negative impacts on pollution, rather they are able to promote the microbial diversity of the soil all the while granting a better fertilization: Geng and coworkers[12] systems affected the soil fertility up to a depth of 60 cm, while keeping unvaried the 60–100 cm range.

Concerning the incomplete uptake of both pesticides and fertilizers by the plants, a relationship between the residues and phosphorus loss

* Corresponding author.
** Corresponding author.
*E-mail addresses:* fabio.pizzetti@polimi.it (F. Pizzetti), filippo.rossi@polimi.it (F. Rossi).
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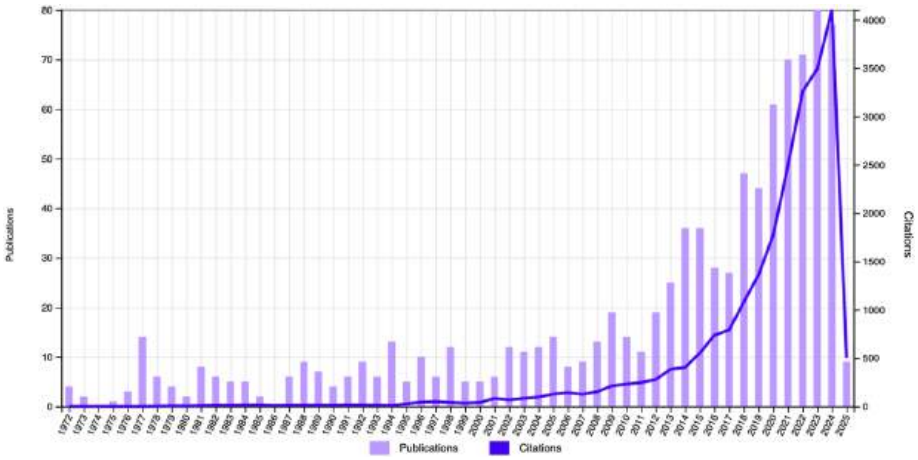


**Fig. 1.** Number of articles and citations on controlled release system for fertilizers and pesticides. Source Web of Knowledge.

from the vegetation was highlighted.[14] These phenomena underline another crucial concern for sustainability, since the residues could filter throughout the soil and contaminate water-body like rivers and ponds, while also contributing to the water eutrophication problem.[14] Looking at the literature of the past years there seems to be the need of a comprehensive work that takes into account the new slow release solutions and organizes the outputs in an effective way (Fig. 1). As such, our work aims to sift through the main delivery systems present in literature and to make a preliminary separation according to the size of the solutions, dividing them into three main categories: nanostructures, micro-structures or macro-structures. Even if the performances expected from fertilizer release systems and pesticide release ones are different in this work we aim to collect all the possibility to allow their sustained and prolonged release from a materials point of view. The main difference resides in the fact that pesticide molecules are extremely hydrophobic and toxic for the environment and so strong attention on its solubility and protection is fundamental. In the case of urea the problem resides in its high hydrophilicity and SRSs can help to optimize and control its administration to the plants. The different SRS are dimensioned and separated in subparagraph in accordance to their nature, allowing us to describe the general systems with the unique traits of each of them and to have a better comparison of the efficiency of the systems themselves.

## 2. Release mechanisms

Before examining each type of controlled release system and the materials involved, it's crucial to grasp the mechanisms that allow a fertilizer or pesticide molecule to be gradually transported from the matrix into the surrounding environment. The release rate can typically be managed through diffusion, degradation, or osmosis. In most cases, diffusion acts as the primary release mechanism, occurring through water molecules occupying the pores and relying on the porous structure of the matrix. When water seeps through the coating layer and fills these pores, it gradually shifts the active ingredient toward the surface, resulting in a controlled release. Factors such as membrane thickness and water solubility further influence active ingredient outflow. The release rate follows zero-order kinetics, assuming that the system's physical attributes and dimensions remain constant during release with no polymer loss or degradation. Additionally, this model presumes there is no burst release. Self-diffusion coefficients can be estimated through nuclear magnetic resonance. Osmosis-controlled and swelling-controlled releases depend on osmosis, where water flows across a selective membrane governed by a pressure gradient. In this scenario molecules move outward due to the pressure gradient, controlled by the diffusion coefficient of the active ingredient and polymer chain relaxation. For water-soluble pesticides, matrices are used for their swelling behavior due to hydrostatic pressure. When placed in water or buffer solutions, the solvent diffuses into the polymer network, causing swelling and volume expansion. This swelling is characterized by two moving fronts: the swelling interface moving inward and the polymer interface moving outward upon contact with water. The cargo release depends on chain relaxation and/or drug diffusion rate through the polymeric system. Another diffusion type occurs through polymer diffusion where solute motion through the matrix controls the process. The release is generally amplified by matrix porosity, which increases surface area for active ingredient dissolution.

Here, diffusion rate relies on physical pesticide parameters like size, morphology, and water solubility. Surface erosion or degradation of the polymer matrix leads to release where zero-order surface release determines the rate-limiting step. This process combines surface dissolution and erosion at the polymer surface. Surface erosion is preferred due to reproducible erosion kinetics, offering controlled delivery while protecting sensitive active ingredients. Conversely, bulk erosion is less predictable and fails to safeguard pesticides from environmental exposure, making it less ideal for controlled release systems.

## 3. Nanostructures

Hereafter, the nanodelivery term is used to describe structures comprising of a size smaller than about 500 nm. Among the systems found in literature the main ones feature direct coatings of substances, emulsions, micelle, fibers, nanoparticles, metal organic frameworks and other novel systems under study.

### 3.1. Nanocoatings

The simplest system for controlling the release of fertilizers is to use a coating on the particle itself as barrier able to limit contact between water and the fertilizer. The coating could either be inorganic or organic.[5,15] Some examples of the inorganic ones are represented by sulfur-based and mineral-based (like zeolite) coatings.[16,17] On the other hand, the organic materials features chitosan, starch, cellulose, agricultural residues, lignin and thermoplastic materials like the superabsorbent polymers, which are sought-after for their remarkable ability to absorb moisture and to retain substances. Among the factors affecting the release profile of coated substances, temperature and pH have a major role, where a temperature increase has an effect on the nutrient solubility, while for pH the release is enhanced by alkaline values thanks to the increase of the swelling capacity.[18]

Other parameter affecting the transmission rate are the size and shape of the fertilizer, where a smooth round geometry is preferred, as well as the soil characteristics: pH, temperature, composition, moisture

and microbial activity.[18] In practice, natural polymeric coatings are favored thanks to their non-toxic and biodegradable characteristics. Besides, they represent a low cost and easily-implemented solution. In the scope of natural polymers, in literature two formulation are proposed and implemented on a crop production in a greenhouse model[19] on tomato plant growth.[20] Salimi and coworkers[19] used a starch-g- poly (styrene-co-butylacrylate) latex with natural char reinforcement as a coating for urea nanoparticles with a mean thickness in the range 80–110 nm. The experiment showed nitrogen release in water dependent on the starch and natural char (NC) composition: starch's hydroxyl groups formed H-bonds interactions with urea, restraining the fertilizer release. In Fig. 2 the synthetic mechanism of starch-based nanoparticles is visible together with SEM images at different magnification.

Moreover, natural char functional groups can interact with the polymer starch-matrix and can create tortuosity in the matrix geometry for the water passage, enhancing the coatings barrier properties. As such, increasing quantities of both starch and natural char affected positively the coating barrier properties. Similar performances were evaluated by using a coating of starch-g-poly(styrene-co-butylacrylate) latex reinforced with natural char for NPK fertilizer release.[20] Moreover, in their study the chitosan nanographene oxide coating was also synthesized for iron and zinc slow release.

In both formulations the nutrients were absorbed more easily by the plants, showing improved growth compared to the control groups.

### 3.2. Nanoparticles

In agricultural applications, bio-polymers represent a sustainable solution for long term releases, thanks to their biodegradable and biocompatible nature. Among these, chitosan, alginate, zein and polylactic acid are the polymers most frequently used.[21] In literature some solutions are developed using chitosan in combination with other polymers or minerals to develop frameworks that are able to deliver continued quantities of fertilizers and pesticides in the long-term.[22–25] In particular, Abdel-Aziz and coworkers[22] studied the influence of chitosan poly-methacrylic acid nanoparticles on the delivery ability of NPK in sandy soil experiments (dimension between 17 and 25 nm and stability influenced by the presence of salts that can decrease the colloidal electrostatic stabilization). They found that the best performances were obtained with nanoparticles loaded with 10 % of NPK in terms of

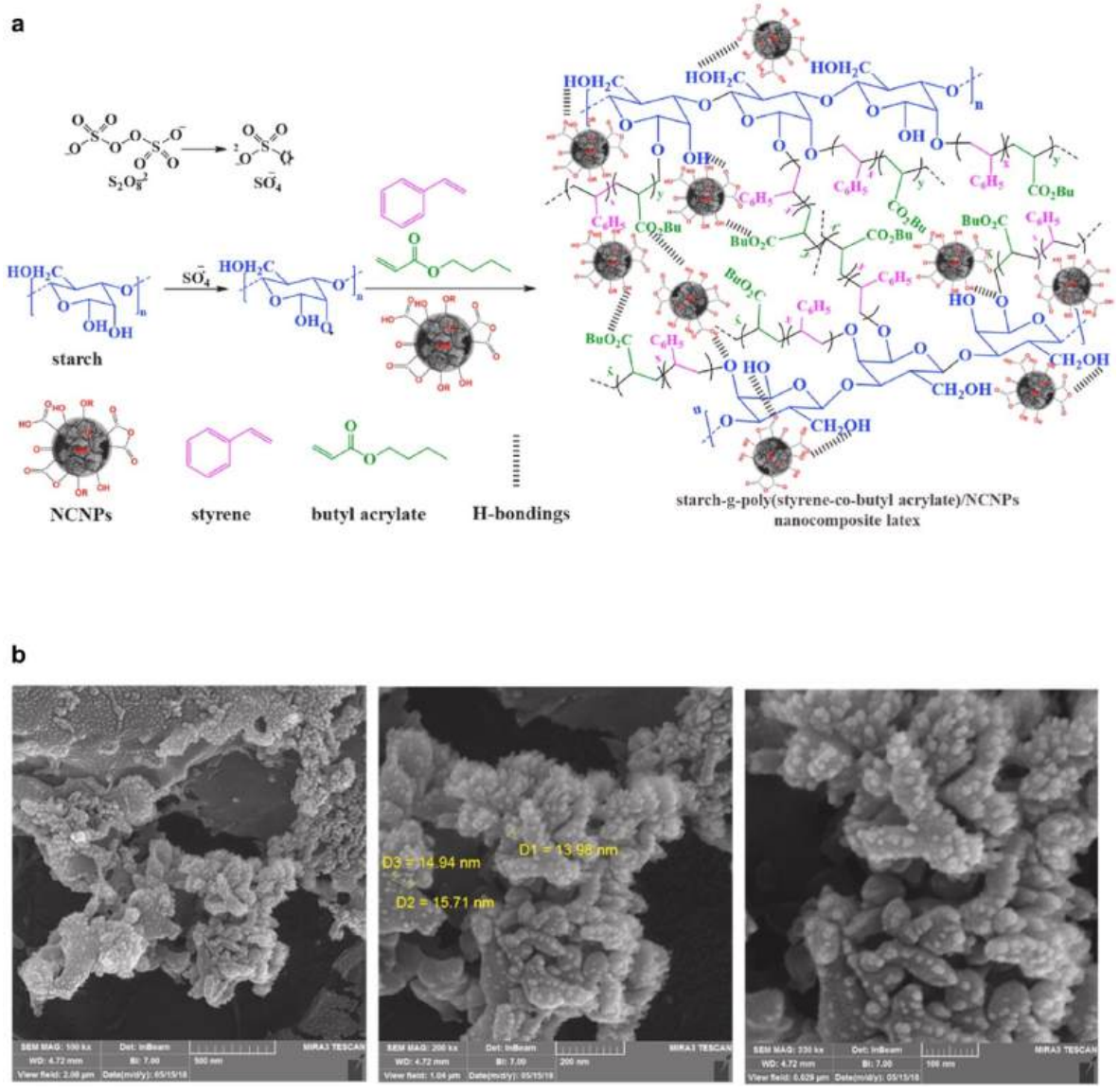


**Fig. 2.** (a) Schematic representation of synthesis mechanism and (b) Scanning electronic microscopy images of the starch-g-poly(styrene-co-butyl acrylate)/NCNPs nanocomposite, in different magnifications. Reprinted with permission from Elsevier.[19]

number of germinated spikelets, root length and foliar length. Also, using chitosan poly-methacrylic acid nanoparticles the time needed to reach the harvesting stage was reduced by 23.5 %. On the other hand, the release of pesticides did not produce remarkable results due to their high hydrophobicity. Ma and coworkers[23] used a carrier material of chitosan oligosaccharides and gelatin for dinotefuran nanopesticides delivery (size approximately 170 nm), which demonstrated better performances compared to the control group only with small percentages of pesticides loaded. The encapsulation within the device can guarantee strong photostability to the final nanosystems. Additionally, other systems with clay, chitosan and iron(III) demonstrated similar performances to the control group, while also guaranteeing a longer term release. In the case of lignin, a possible application is suggested by Zhao[26] where they prepared lignin nanocarriers characterized by an enzyme responsive system against root-knot nematodes (average particle size of 300 nm).

Since nematodes produce enzymes after the digestion of plant's roots, the implementation of an enzyme responsive system permits the nanocarriers to release higher quantities of pesticides in the presence of the target pest: after 51 h the release was 96 % and 73 % in presence of enzymes and without enzymes, respectively. The targeted release showed promising results, featuring a mortality rate of 90 % against the 54 % for the original pesticide application. This approach can also guarantee better protection of the hazardous molecules and so to limit the toxicity directed to the other species. Other lignin nanocarriers application are found in the transfer of pesticide to soybeans roots.[21] In this case, the release profile showed a temperature dependent diffusion: 90 % was released after 80 h at 25 °C, while they found a complete release after only 20 h at 37 °C. To verify the compatibility of lignin implementation in real life applications, field trials were also performed: Zhang and coworkers[27] used lignin-modified epoxy resin nanocapsules (negatively charged, average particle size 150 nm) to deliver abamectin pesticide against root-knot nematodes, obtaining excellent performances thanks to the improvement of the pesticide stability and mobility in the soil guaranteed by the nanocarriers and their coating. Moreover, the slow release attained permitted a higher inhibitory effect on the target pests and on the eggs. Continuing with the zein material, some easily-prepared zein nanoparticles (average size approx. 80–100 nm and high stability at pH between 5 and 9) are reported in literature, where they present an increased insecticidal effect[28] and an augmented transfer of pesticide particles to the roots, leaves, stems and plant tissue over time compared with the controls in the application of low and medium pesticide concentrations, while only prolonging the release for high concentrations.[29] More complex systems with better performances exist in literature: Zuo and coworkers[30] proposed a double-shell system where the emamectin benzoate (EB) pesticide is stored into the inner β-cyclodextrin core through hydrophobic interactions and a second shell of amino-functionalized zein which encapsulates the β-cyclodextrin layer using electrostatic and hydrogen bonding interactions (negative surface charge and approx. size of 157 nm). This system permits a slower ultraviolet (UV) degradation of EB, which remains in a concentration 1.5 higher in the double-shell particles compared with the controls after 180 h.

Moreover, the β-cyclodextrin (β-CD) core showed better encapsulation efficiency compared to the only zein capsules, while the amino-functionalized zein layer guaranteed higher amphiphilic properties to the system and so a higher dispersion capability of the pesticide with consequent higher colloidal stability.

This solution is also characterized by an enzyme responsive release, where the β-cyclodextrin core is broken by the enzymes leading to higher release rates. In particular, the nanoparticles were treated with neutral protease and α-amylase enzymes: a pronounced response was shown by the group treated with the α-amylase enzyme, where the release was enhanced by 28.8 % compared to the 2.1 % enhancing of the

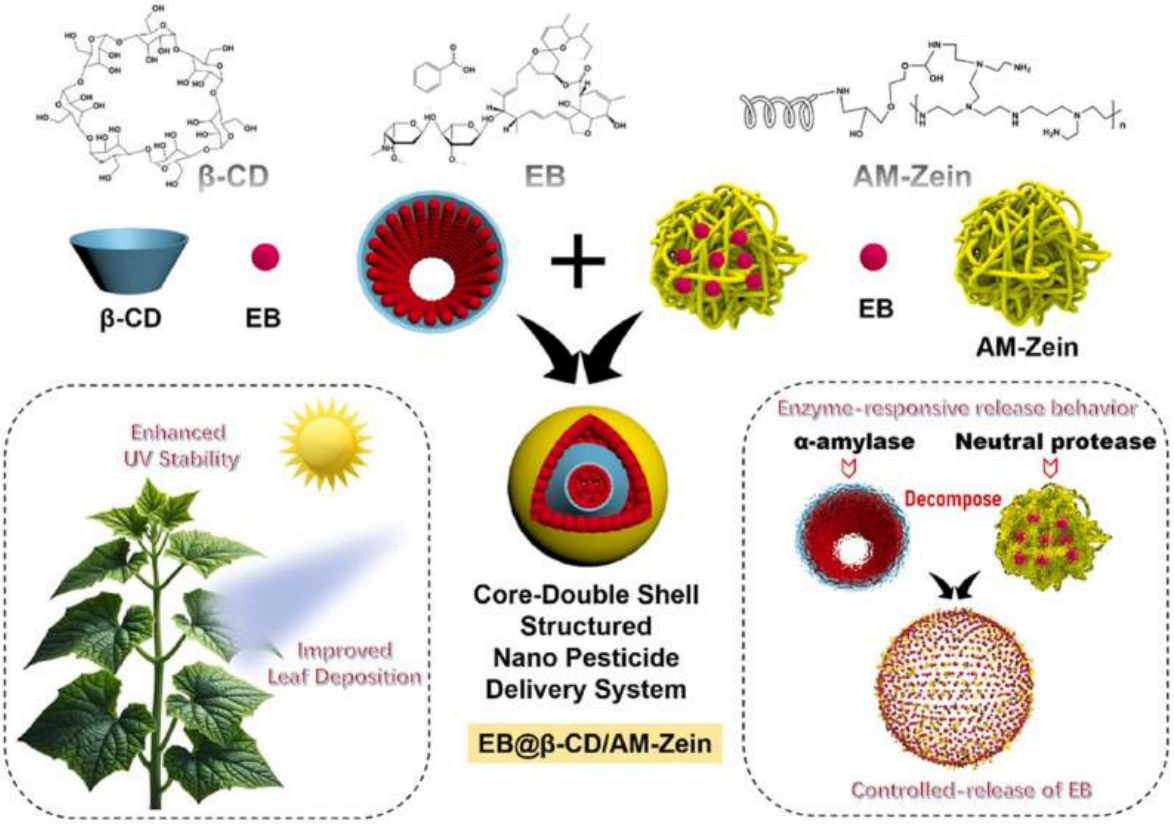


**Fig. 3.** The preparation schematic of the core-double shell structured nano pesticide delivery system EB@β-CD/AM-Zein and its enzyme-responsive release behavior and enhanced UV stability during application process. Reprinted with permission from Elsevier.[30]

neutral protease group. In Fig. 3 the schematic preparation of the core-double shell structured nano pesticide delivery system and its enzyme-responsive release behavior together with enhanced UV stability during application process is visible.

Regarding poly-lactic acid (PLA), Shen and coworkers[31] used PLA nanoparticles for lambda-cyhalothrin (LC) pesticide release, which presented a sustained release dependent on the LC and PLA ratio: the cumulative release decreased according with lower LC to PLA ratios (approx. dimension 200 nm). The 1:1 performed 89 % content release after 240 h, while the 1:4 reached only the 57 %. Moreover, PLA nanoparticles permitted a better foliar adhesion and retarded the UV degradation compared to the technical lambda-cyhalothrin degradation: after 72 h only the 20 % was degraded compared to the 83 % of the technical one. Similar performances were attained by the pyraclostrobin pesticide release from PLA nanoparticles, where 84.47 % of pesticide was released after 25 h.[32] An enhanced mortality rate was also attained using avermictin B1, a loaded polysuccinimide, with glycine methyl ester nanoparticles with consequent increase between 10 % and 20 % according to the pesticide concentration.[33] The same trend based on the loaded pesticide concentration was found in poly(lactide-co-glycolide)-b-poly (ethylene glycol) methyl ether (mPEG-PLGA) nanoparticles (approx. dimension 120 nm, high stability in soil): high inhibition rates were obtained using low and medium concentrations, while at higher concentrations the trend was inverted.[34] These performances highlight the potential of these systems for long-term release implementations and target release. Another widely used application of nanoparticles is represented by the mesoporous silica nanoparticles. Their long term release was found to have an active role in regulating the pests population[35] and also preventing insects oviposition.[36] Silica nanoparticles had excellent tunability thanks to the coating thickness and stimuli-responsive behavior, which permits a greater delivery of both pesticides and fertilizers.[37,38] For example, field experiments reported increases in the watermelon yield of more than 70 %[39] and a reduction of 71.67 % in the nodules number in a cucumber plant experiment.[35] A comparison of some of the silica nanoparticles application found in literature is presented in Table 1.[40–47]

These solutions present a responsive release to pH, temperature, redox and enzymes, permitting the evaluation of the best profile to counter different target organisms. Other polymer applications can be found in literature. Star polycation particles were employed to deliver gene silencing systems to inhibit pest growth[48] and as nanocarriers for thiamethoxam.[49]

In both cases an increase in the mortality rate of the target organisms was observed, effect made possible due to the slow release of the pesticide in response to the presence of the target organisms. Some cost-effective solutions feature the nanoparticles composed of acidic and lactonic sophorolipids to deliver lambda-cyhalothrin, a pesticide which technically reaches the 90 % of release in just 8 h, over a timeframe of 30 h[50] and the styrene and methacrylic acid particles that showed a sustained release and an increased foliar retention rate.[51] Good results were also reached by Shi and coworkers[52] using polydopamine nanoparticles loaded with emamectin benzoate insecticide (approx. dimension 160 nm). These carriers displayed significantly increased leaves adhesion and UV-resistance properties, while also guaranteeing a prolonged release in a period over 200 h, Where the cumulative release only reached 29 %. The rate of insecticide release could be tuned taking benefit from their pH responsive features, thanks to which the cumulative release after 120 h was 75 %, 27 % and 14 % at pH 5, 7 and 9, respectively. Overall, nanoparticles appear to be the most common nanocarrier system present in literature, since they can rely on different environment-responsive signals and they show great potential for target pest management and nanoscale substances transfer to plant's roots and leaves, all the while ensuring non-toxicity to non-target organisms and bio-safety. Considering different type of applications, other systems were formulated: in the instance of a foliar spray, nanogels were synthesized to achieve better wet-ability, improve adhesion and increase the washing resistance.[53] For the release of both pesticides and fertilizers on the long run, some specific systems were produced. In particular, the use of lignin and chitosan nanocomposites for the delivery of urea showed a continuous release up to the 75 day,[54] while the incorporation of hydroxyapatite and fertilizers in a hydrogel composed of cellulose-graft-poly(acrylamide) polymer guaranteed a release up to 16 weeks based on the velocity of the polymer degradation performed by the soil bacteria.[55]

### 3.3. Metal organic frameworks

Metal organic frameworks (MOFs) are structures formed by the interaction via coordination bonds between organic ligands and inorganic metal ions that act as the nodes of the structure.[56,57]

They present a porous crystalline frame that enable them to act as effective carriers for a sustained release and, considering their wide surface area, they display high loading yields. Moreover, the coordination bonds are of moderate strength, making the structure prone to biodegradation.[58,59] In literature, MOFs have gained attention not only in the biomedical field for their unique properties, but also in agriculture implementation for the release of both fertilizers and pesticides. Liang and coworkers[60] propose a pH responsive MOF composed by a metal organic frame (MIL-101(Fe)–$NH_2$) loaded with chlorantraniliprole (CAR) molecules. Afterwards, the nanoparticles are coated with carboxymethyl starch to block the structure's pores via covalent interactions. The particles presented a uniform diameter around 351.7 nm and had an octahedral morphology characterized by a rough surface. In terms of pesticide release, the nanoparticles showed a marked response to the ambient pH: the CAR cumulative release was 13.67 %, 8.47 % and 85.85 % at pH 6.0, 7.0 and 10.0, respectively. This result was attributed to the system instability in alkaline conditions, where a gradual degradation of the MOF take place, leading to a higher content release. A subclass of MOF features the zeolitic imidazolate networks (ZIFs) which have a structure similar to zeolites, porous materials built of a crystalline

**Table 1**
Main characteristics and performance comparison of silica nanoparticles releasing systems.

| Size | Coating/Grafting | Responsiveness | Loading efficiency | Release rate | Ref. |
|---|---|---|---|---|---|
| 320 nm | N-isopropylacrylamide and CS | Temperature and α-amilase | 30.87 % | 7.2 % and 45.8 % at 14 days | 38 |
| 102 nm | Zein | pH and redox | 24.7 % | After 154.5 h at pH 5, 7 and 9: 14.2 %, 9.8 % and 23.6 % | 39 |
| <100 nm | Cellulose | pH | 12.41 % | After 7 days in presence of cellulose, glu- tathione and both: 60.84 %, 16.54 % and 73.46 % | 40 |
| 125 nm | Tannic acid and chitosan | pH and chitinase | 16.58 % | After 72, at pH 5, 6, 7 and 9: 38.07 %, 28.03 %, 10.69 % and 9.64 %. With 0.01, 0.05 and 0.10 $U/g^{-1}$ of chitinase: 86.91 %, 89.76 % and 91.93 %. | 41 |
| 150 nm | | pH and temperature | | After 200 h, at pH 5, 9 and 7: 75 %, 65 % and 50 %. After 200 h at 45 °C, 35 °C and 25 °C: 90 %, 90 % and 50 %. | 42 |
| 20 nm | Chitosan | pH | 84 % | After 72 hatpH 6.21, 6.94 and 7.89: 33.33 %, 36.2 % and 44 % | 43 |
| 150 nm | Chitosan | pH and redox | 23.7 % | After 15 days at pH 7 and 5: <20 % and 39.17 % | 44 |
| 187 nm | | pH | | After 48 h at pH 4.8, 7.2 and 8.9: 62 %, 68 % and 84 % | 45 |

regular net-work of alumina and silica tetrahedron.[61] A possible classification of ZIFs is given by the size of the widest pore: small pore with less than 8 rings, medium pore (up to 10 rings), large pores (up to 12 rings) and extra-large pores with more than 12 rings.[61] In the case of zeolitic imidazolate framework-8 (ZIF-8), the framework is composed by the interaction of 2-methylimidazole with zinc and cobalt ions, ending in a sodalite cage geometry. Moreover zeolitic imidazolate frameworks showed high loading efficiency and sustained long-term release behavior.[62] All the ZIFs found in literature showed high porosity and large surface areas, properties which promote molecules loading in the ZIF particles, and they also had good thermal stability.[63–65] Ren and coworkers[63] conducted release experiments using a ZIF-8 composite loaded with dazomet (DZ) pesticide. The DZ@ZIF-8 particles showed a pronounced pH response: at lower pH values, around 3.5, the DZ cumulative release was higher than the one at 4.8 after 24 h, all the while at a pH of 9.5 it reached 23.16 % only after 60 h.

Moreover, the in vitro experiment revealed a fungicidal activity 36.3 % higher than the one of the pure pesticides, while the pot experiment demonstrated that the pesticide was slowly released and it did not incur in a premature degradation, unlike the pesticide employed alone (Fig. 4). In Fig. 4 the results discussed were visible together with microscopic images on the ability to change conformation and consequently the release performances that can be obtained changing the pH and moving to the acidic environment. Similarly, Ma[65] used dinotefuran (DNF) encapsulated in ZIF-8 particles for pesticide and $Zn^{2+}$ micronutrients release. They featured a delivery up to 32 days in soil and a pH responsive behavior: $Zn^{2+}$ cumulative release reached 18.6 %, 3.6 % and no obvious release at pH 5.0, 7.0 and 9.0 respectively; while DNF had 76.5 %, 54.9 % and 50.7 % substance release at pH 5.0, 7.0 and 9.0. The DNF release from ZIF-8 after 72 h kept a 96.6 % efficiency, against the 63.3 % of the pesticide alone and showed an excellent UV degradation resistance. A corn growth experiment was also performed, where the plant height, root length, fresh and dry weight were measured, revealing significantly higher measurements for the ZIF- 8 samples with an increase of 18.44 %, 3.84 %, 20.12 % and 29.69 %, respectively. Lastly, Huang and coworkers[64] encapsulated the fungicide prochloraz (Pro) and the growth regulator diethyl aminoethyl hexoanoate (DA-6) in ZIF-8 carriers, then they grafted siRNA-targeting PGase using electrostatic

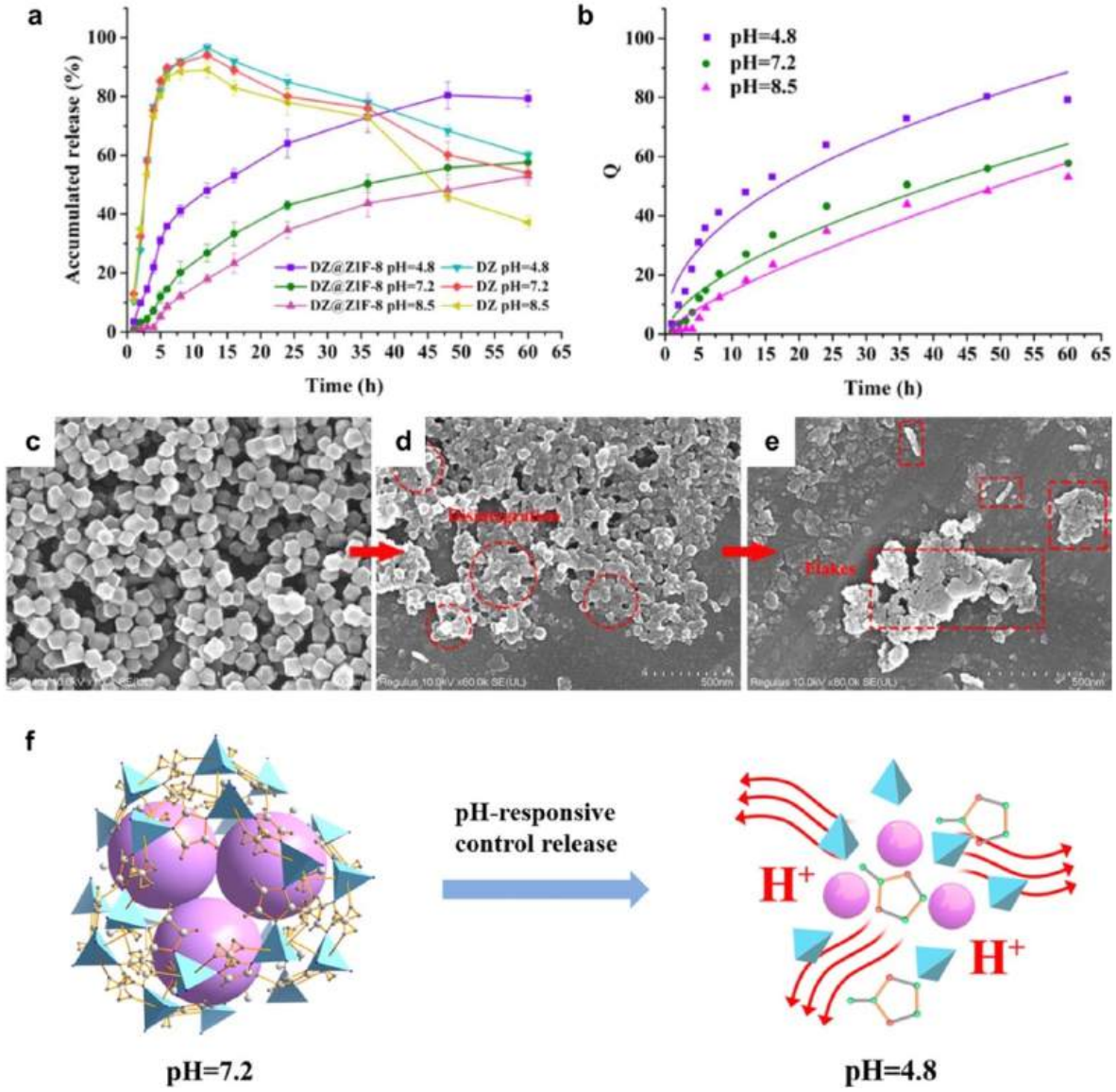


**Fig. 4.** (A) Accumulated release of DZ from ZIF-8 and (B) fitted plots with the Peppas model at different pH values of 4.8, 7.2, and 8.5. (C–E) Scanning electronic microscopy image of DZ@ZIF-8 in an acidic aqueous solution and (F) schematic diagram of the pH-responsive control release profile. Reprinted with permission from American Chemical Society.[63]

adsorption on the nanoparticles, reaching a dimeter of 841.7 nm. Pro release showed a pH induced release with 49.5 %, 48.9 % and 73.9 % after 168 h at a pH of 7.0, 9.5 and 4.5, respectively. Moreover, the loaded Pro molecules displayed perfect storage stability. For what concerns the siRNA, the ZIF-8 nanoparticles performed a sustained release over time and were able to silence the target gene expression, featuring a reduction of 48.5 %. At last, the nutritional efficacy was evaluated: the growth height and root length of rice seedlings were measured at day 7 and 14, showing better performances than the ones treated with the loaded ZIF-8 nanoparticles in both cases, and the leaves appeared greener. Overall, metal organic and zeolitic imidazolate frameworks appear to be innovative and highly performing nanoscale solutions for both fertilizer application and pesticides release for pest management.

Their biodegradable and pH responsive structure is ideal for soil application where fungi and pest digestion produce acidic substances, affecting the ambient pH.[64] They all showed good thermal and storage stability, making their commercialization possible on a large scale.

### 3.4. Micelles

A micelle is a particular form of aggregate formed when amphiphilic molecules, composed of a hydrophilic and a hydrophobic side, gathers when in contact with water.

The hydrophilic polar heads place themselves at the interface with the water, usually arranged in a radial geometry to reduce as far as possible the contact between the hydrophobic tails and the water phase. In agricultural application, micelles are often used as carriers for lipophilic pesticides and for the regulation of their release, considerably prolonging pesticides release and alleviating the problem of water eutrophication caused by the filtration of dangerous compounds into water sources. Moreover, thanks to their stability in low concentration solutions, their employability widens to the spray application over leaves, where they often show improved wettability, spreadability and interfacial deposition.[66] From this perspective, a chitosan derivative (N-deoxycholic acid-O-glycol chitosan) was evaluated as a carrier for rotenone pesticide.[67] The formed micelles presented a spherical size in the range of 67.5–83.3 nm in the dry state and they had critical micelles concentration equal to 0.051 mg/mL. The self-aggregation remained stable in the water environment and the release profile showed an initial burst after the first 10 h, which continuously progressed until the complete release after 70 h compared to the 29 h for the rotenone in free form.[67] Similarly, Li and coworkers[68] formulated a polymeric micelle with reactive oxygen species loaded with validamycin pesticide. Micelles size was investigated under digital light scattering, resulting in a mean diameter of 235.60 nm in dry conditions, and around 800 nm after their swelling in water for 12 h as visible in Fig. 5. In addition, the ROS response was evaluated using a solution of $H_2O_2$ showing a higher swelling after the same amount of time, corresponding to a mean size around 1200 nm. Moreover, the release percentage increased according with the increment in $H_2O_2$ concentration (Fig. 5). In particular considering 80 μM of $H_2O_2$ the release is almost complete after 120 h while for 40 μM it reached a plateau value around 60 %.

This formulation proved to have an increased control efficiency of 162.19 % compared with to the control validamycin pesticide release.[68] In contrast to this results, triple responsive micelles sensitive to enzymes, redox and alkaline conditions presented herbicidal efficiency comparable to the technical pesticide, even though increasing the herbicide stability and protection towards light.[69] Good results were attained by Yang and coworkers[70] with azobenzene derivate nanoparticle coated with γ-cyclodextrin. The azobenzene particles had a photosensitive behavior, attaining higher release per-centages with light exposure: 85.4 % after 120 min of ultraviolet (UV) exposure, 88.32 % and 89.65 % after 60 and 90 min of sun exposure. Instead, when kept in a dark environment, the cumulative release reached 20.5 % after 150 min.

This decrement in release percentages was due to the fact that when exposed to light the vesicles undergo a rupture of their structure imparted by the conversion of the azobenzene from *trans*-to *cis*-conformation. In general, nanomicelles present unique properties for the sustained release of pesticides, as it was showed by a binary additive pesticide system which was able to improve both the deposition and retention of the loaded substance, meanwhile demonstrating also an anti-splash behavior.[66,71]

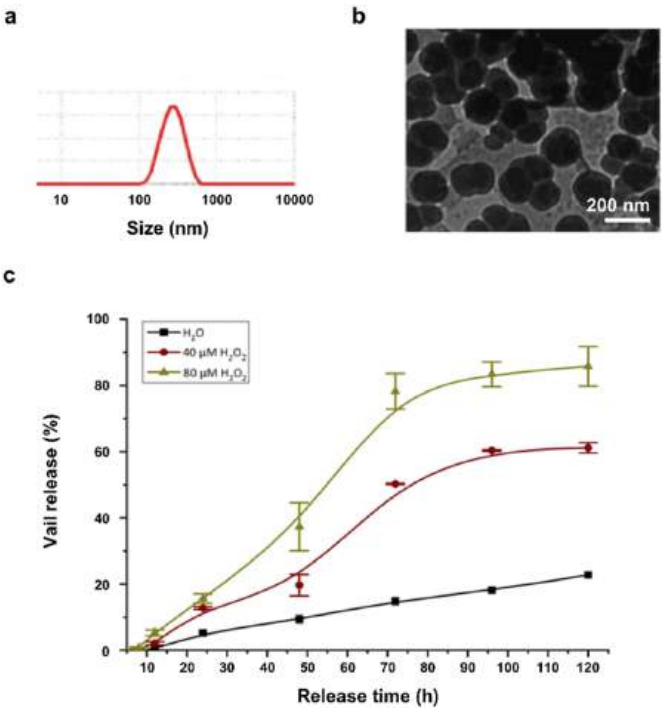


**Fig. 5.** a) Morphology of polymeric micelle was characterized by dynamic light scattering and b) transmission electron microscopy image; c) release profiles of Vail-loaded polymeric micelles in the presence of different concentrations of $H_2O_2$. Reprinted with permission from American Chemical Society.[68]

### 3.5. Nanoemulsions

Nanoemulsions present great properties that make their deployment perfectly suited to be used as sprays, specifically for the foliar application.[72,73] They can be employed as pesticides carriers, since they do not affect their form and stabilization.[74] Moreover, better bio-activities than the raw pesticides have been reported in literature, in addition to safety assurances to the use over crops and to non-target organisms.[73,75] This is due to the fact that the nanoemulsions provided an increased wet-ability and enhanced the adhesiveness to the leaves, as well as they promoted the pesticide penetration in the crops leaves.[73,76] On the downside, dilutions can hinder the actual field employment since the emulsions tend to aggregate over increasing dilution volumes.[75] The formulations presented in literature shows good storage performances and they tend to be cost effective.[73,77] For instance, Modafferi and coworkers[72] present an oil in water emulsion of garlic essential oil (EO), which composition features a high concentration of EO (15 % w/w), the surfactant Tween 80 (poly-oxyethylene (20) sorbitan monooleate) (5 % w/w) and double-distilled water (80 %). Their stability was verified and they kept good polydispersity index (PDI) throughout a period over 1 year: the PDI was 0.05 ± 0.01 right after the preparation, 0.12 ± 0.025 after some months and 0.17 ± 0.02 after one year. Moreover, in a later study they compared with the toxicity of the pesticide in emulsions produced through high energy processes like sonication, high-pressure homogenization or high-pressure micro-fluidization compared with the raw emulsions: the processed emulsions attained 100 % toxicity against the target organisms compared to the inefficiency of the raw emulsions.[78]

For what concerns the release profiles, the avermectin (AVM) pesticide-castor oil based polyurethane (CO-PU) emulsion developed by Zhang and coworkers[79] presents an initial burst release, followed by a steady release over time at every tested temperature, although the trend increased with increasing temperature. At temperature over 35 °C they presented an almost complete release after 72 h, all the while at 25 °C the cumulative release reached 54 % after 72 h and reached almost 80 % after a total of 180 h. The release profile also followed a pH dependent behavior, with a faster rate in acidic conditions, where the cumulative percentages were 99.6 % at pH 4 and 94.1 % at pH 10 after 120 h (Fig. 6). The formation of the nanoemulsion starts from the mixing of water loaded with CO-PU latex particles and acetone then followed by a step of solvent evaporation. Similar results were found by Kumar[80] with two different emulsions composed of eucalyptus oil and a mixture of Tween 20 and Span 80 surfactants in different ratios. The emamectin benzoate pesticide was loaded in the eucalyptus oil core. After 24 h the commercial pesticide attained a release over 99 %, while the two nanoemulsion formulations reached 50.42 % and 37.52 %. Values comparable to the castor oil based emulsions were found: after 180 h the cumulative releases amounted to 72.64 % and 63.53 %, compared to the 80 % of the other study. To summarize, emulsion systems are able to sustain prolonged releases in period of time over the 180 h and with a stability that ranges from months to over a year according to their formulation and optimization. The privileged application of this type of systems is the spraying over leaves, paying attention to the degree of dilution necessary to avoid their coalescence, since nanoemulsions are able to provide enhanced adhesion properties and, nonetheless, enabling a better penetration of the pesticides in the crop's leafage. Also Pickering emulsions represent a valid alternative. In this direction a pesticide delivery system formulated by J. Tian et al.[81] consist of a Pickering emulsion (O/W) with foliar affinity. The oil part is consisted of tea tree oil loaded with avermectin. Zein was used to improve binding with sodium abietate, thanks to non-covalent binding. The formulated system was able to release 2.4 times slower compared to the commercial emulsion, without compromising the insecticidal and antibacterial activity.

### 3.6. Nanofibers

Nanofibers are used as carrier systems in the agriculture sector demonstrating to be biodegradable and non hazardous for both heterotrophic bacteria and fungi.[82] The use of nanofibers with agrochemicals is generally compared with nanocoating demonstrating to be more effective. Indeed nanofibers allowed a more controlled and sustained release of fertilizers and greater gas circulation, unlike nanocoatings.

When exploring the use of electrospun fibers as a seed coating, they confirmed that the polymer used as a coating did not affect the physiological quality of the seeds facilitating the water absorption, accelerating the imbibition process and consequently increasing the germination and providing better protection during storage. Electrospinning is one of the most widely used strategy to produce nanofibers thanks to their easy scale up and low cost.[83] An example is given by Zn-loaded poly(butylene-adipate-co-terephthalate) nanofibers that reached the maximum release, 40 %, after 6 h and remained at a plateau for all the tested 240 h.[84] Only after the fibers degradation the release increased to 100 % but this did not guarantee a sustained slow release. Another example is shown by single and double-layered hollow PLA nanofiber yarns: after 12 h the cumulative release attained percentages of 79 % for the single layer and 24 % for the double one, but no relevant increase was seen during the experiment duration (over 400 h).[85] Better results were obtained with PLA in combination with urea to prepare fiber materials using coaxial electrospinning with prolonged release time over 80 days.[86] Good results were obtained also with other fertilizers as obtained by Sharma[82] with cellulose fibers loaded with nitrogen-based fertilizer: the initial burst reached 30 % of release after 1 day and the fertilizer was continuously released up to a percentage of

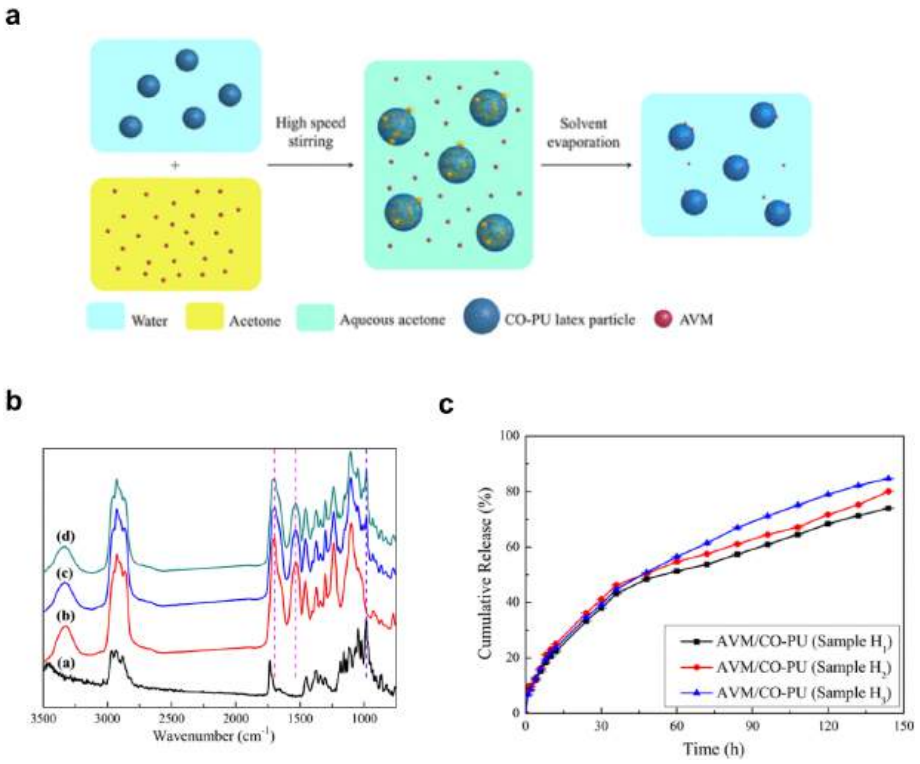


**Fig. 6.** a) Illustration of the synthesis of AVM/CO-PU nanoemulsions; b) Fourier transform infrared (FTIR) spectra of (a) AVM, (b) CO-PU carrier, and AVM/CO-PU drug-loaded system (c) sample $H_2$ and (d) sample $H_4$; c) Release curves of the different AVM/CO-PU nanoemulsions at 25 °C and pH 7.2. Reprinted with permission from American Chemical Society.[79]

58 % after 8 days. Nanofibers can also be used to build 3D structures like hydrogels. In this direction the hydrogel obtained demonstrated great potential for agricultural application thanks to its optimal blend of natural polysaccharides which met the necessary criteria like biocompatibility and biodegradability. The synthesized hydrogel showed a remarkable capacity for water absorption and excellent ability to retain water. The loading capacity of urea was demonstrated to be 92 % in terms of efficiency with exceptional urea encapsulation performance and slow regulation of urea discharge with a significant positive impact on both seed germination and plant growth.[87] Even if great efforts have been made to obtain coated fertilizers with more efficient nutrients release, the development of simple processes using greener materials is still challenging. In this field the design of biobased formulations, prepared using biochar materials and oxidized cellulose nanofibers filled into methyl hydroxyethyl cellulose can be used as coating agents of phosphate fertilizer (triple superphosphate).

These findings indicate that the biobased developed nanocomposite formulations of cellulosic biochars are suitable to produce slow-release phosphate fertilizers with reduced leaching and water-saving properties.[88] Polymers can also be added with inorganic molecules, like $TiO_2$, to introduce further properties. The addition of $TiO_2$, can potentially suppress the hydrophilic properties of the membranes made of polyvinyl alcohol increasing the release rate.[89] Similarly Kumar and coworkers[90] built a film made of a polyvinyl alcohol (PVA)-starch substrate loaded with Cu–Zn releasing carbon nanofibers with a thickness of 0.5 mm. The film was then cut into smaller pieces and mixed with soil in a pot experiment with different film-soil ratios and the best performances were given by the pot with the film in a concentration of 4 g/kg of soil. The germination percentage reached 96 % and the plants had an increase in height of 83 % compared to the control group. Overall, coupled systems proved to be adaptable to different scenarios for both the delivery of pesticides and fertilizers, reaching extremely long term release and improving the delivering of substances, although their complexity could require longer terms for production and could potentially turn to be more expensive than simpler systems. Despite the extremely promising results collected using nanoplatforms strong attention should be dedicated to some critical points. Indeed many studies have mainly concentrated their attention on creating nanostructures with unique properties that improve nutrient uptake and transport in plants. This singular focus overlooks the intricate interactions of nano devices with both biotic and abiotic factors around them and their effect on soil quality. Additionally, since the properties of nanoparticles can be modified in numerous ways, there is significant potential for developing innovative nanostructures, such as those using biopolymers, plant extracts, and microbes. Despite the vast amount of information in this field, it is essential to identify the most suitable nanostructures for specific soil types and further explore their effectiveness through field trials. There is also considerable opportunity to delve into the molecular mechanisms governing their interactions with environmental factors. Moreover, the long-term impacts of using nanostructures on ecosystems and their eventual fate, given that they might undergo chemical transformations affecting their toxicity, warrant attention. Thus, there is substantial room to address multiple research gaps associated with the use of nanostructures in agriculture.[91]

## 4. Microstructures

The following paragraph analyze micro structures for the delivery of fertilizer and pesticide. The spatial variations in both chemical and physical micro structure have a significant impact on the release behavior.[92] To be included in this paragraph the release structure must be within the range of 0.5–200 μm. Lower dimension of this paragraph applies primarily to microspheres and microcapsule, while upper one includes polymers and other techniques, which will be described in the below sections.

### 4.1. Microspheres

The term microspheres essentially refers to empty spherical particles. They can be described as complex system where the payload is homogeneously dispersed, either dissolved or homogeneously suspended. Microspheres are widely used thanks to their high loading capacity, being able to substitute the traditional spreading methods without reducing the amount of the fertilizer, or the pesticide, delivered.[93–95] The functionalization of microsphere is another essential branch to exploit new possibilities of application. When pesticides are sprayed in open systems, the effects of external atmospheric agents can increase the losses. This is the reason why controlled release system are used, indeed the release can be tuned; Wang and coworkers[96] proposed an environmental friendly herbicidal formulation using UV to tune the release, by photoisomerization of cinnamamide units, that reduce the absorption. This is confirmed by the cumulative pendimethalin release result, after 72 h was 86.23 % and 15 %, respectively under sunlight irradiation and in a dark environment. Microspherification can also be used to apply a co-release of two different pesticides, to reduce the risk of resistance and usage frequency.[97] To adjust the physico-chemical properties and chemical composition of the soil, microspheres represent a relevant option. Chitosan is a favorable material to formulate fertilizer release microsphere, thanks to its high biodegradability and excellent mechanical properties.[98,99] The microsphere can be further developed with the addition of potassium alginate and calcium carbonate, to guarantee different degradation kinetics according to pH values[93]; the advantage is therefore to be able to modify the composition of microsphere according to the soil composition.

### 4.2. Microcapsules

Microcapsules (MCs) are often confused with microspheres, indeed the terms are often used interchangeably. But respect to microspheres, microcapsule are heterogeneous particles surrounded by a shell around the core, forming a reservoir.[100] Similar to solution of microspheres, microcapsule can guarantee a slow nutrient release thanks to their swelling[101] and the delivery of the molecules can be tuned with pH, being able to give access to the nutrient only in the desired condition, such as acidic conditions.[102] Alternative tuning options used UV to provide photo-thermal conversion and sequent activation of the active principle[103,104]; in these two studies, the model molecule is avermectin. Huang and coworkers[104] used chitosan and sodium lignosulfonate as wall materials, while chitosan and tannic acid have been used by Li[103]; the use of sodium lignosulfonate and chitosan combined guarantee higher photo-thermal conversion efficiency, 24.03–28.82 %. The slow release of microcapsules can also reduce environmental pollution while maintaining higher stability compared to traditional formulation, so that the pesticide delivery efficiency is increased. The sustainability and low environmental impact is enhanced by the high degradability they are capable of.[105] A common index for the plant stress is the glutathione concentration, a tripeptide with antioxidants properties. Therefore, Wang and coworkers[106] developed glutathione (GSH) responsive microcapsules, delivering pyraclostrobin in an efficient way, testing its antifungal activity against Fusarium graminareum. The sphericity, the smoothness of the capsule can impact on the release properties. In Fig. 7 the synthetic illustration of pyraclostrobin-loaded PU-MCs via interfacial polymerization technique is visible together with the release of pyraclostrobin from the prepared pyraclostrobin-loaded PU-MCs incubated at different GSH concentrations.

### 4.3. Micropolymers

Micropolymer-based systems are easy to be obtained and they are resistant to environmental effects. The polymeric structures present biodegradation properties and, thanks to the action of microorganisms, it can release the active component with greater control.[107]

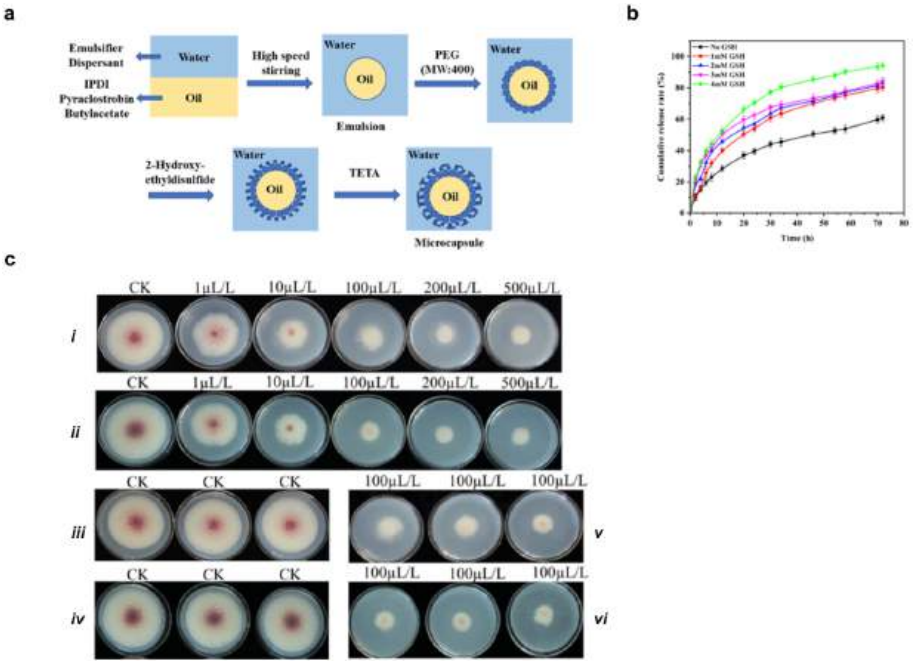


**Fig. 7.** a) Synthetic Illustration of Pyraclostrobin-Loaded PU-MCs via Interfacial Polymerization Technique; b) Pyraclostrobin release rate-time curves of the prepared pyraclostrobin-loaded PU-MCs incubated at different GSH concentrations; c) Fungicidal activities of pyraclostrobin-loaded PU-MCs against *F. graminearum* after 3 days of contact: i) without GSH but with pyraclostrobin microcapsules of different concentrations; ii) with 2 mM GSH and pyraclostrobin microcapsules of different concentrations; iii) cytokinin (CK) without GSH; iv) CK with 2 mM GSH; v) without GSH but with 100 μL/L pyraclostrobin microcapsules; vi) with 2 mM GSH and 100 μL/L pyraclostrobin microcapsules. Reprinted with permission from American Chemical Society.[106]

Polymers can be used as coatings. Liu and coworkers[108] studied different loading of aminated lignin on polyvinyl alcohol, to develop an environmentally friendly urea-based slow-release fertilizer. The system showed good degradability in soil, 51 % weight loss in 45 days. A pot trial with Brassica napus showed how the system significantly enhanced the growth, confirming the release of nitrogen and sulfur as nutrients for the plant. Polymers can also be used as grafting agent, as studied by Riyajana[109] with natural rubber grafted with modified cassava starch using potassium persulfate as catalyst. The swelling ratio decreased in function of the starch used, and the system has improved thermal stability, tensile strength and it easily degrades in soil after the controlled release of urea. High performance liquid starch based mulching materials (LSMM) are an alternative solution regarding grafting and starch. In this direction polyacrylic acid cam be used as a grafting agent,[110] and achieved excellent mechanical and water absorbing properties with germination ratio of lettuce seeds increasing from 60 % in the blank experiments to 84 %.

### 4.4. Inorganic compounds

Inorganic compounds have been developed as vectors for pesticide delivery over the past decade. Clays are an example; the spread ability in the soil is though limited, therefore they must be incorporated into a more complex formulation, either liquid or solid. Chevillard and coworkers[111] incorporated clays with wheat gluten obtaining positive results thank also to a remarkable biodegradability. Clay used was montmorillonite, the pesticide studied was ethofumesate. The organic modified montmorillonites formulation can reduce the ethofumesate diffusivity in soil, while protecting the pesticide from UV degradation. Similarly, a different vector for hydrophobic pesticide can be made of graphene oxide. Combined with PEG the system can increase the water solubility and the resistance to UV. Similarly Song and coworkers[112] formulated a vector with ultra high loading capacity, 1647.2 mg/g, together with an excellent stability during the 2-year storage period. Alternatives are proposed by biochar-based slow-release fertilizers formulation, though still challenging. Here An et al.[113] studied the co-pyrolysis of cotton straw, $K_3PO_4$ and bentonite, using microwaves in a oxygen-limited atmosphere. Sieved and stored with 0.5–1 mm size, diffusion mechanism of P and K got improved slow-release performance.

### 4.5. Microgels

Microgels are an alternative for pesticide controlled release, as demonstrate by Singh[114] proposing a formulation using graft-co-polymerization technique with poly(methacrylamide) on agar-gelatin. Swelling properties are confirmed, as the hydrogel adsorb $4.05 \pm 0.32$ g per gram. The tested linuron herbicide guaranteed a slow and constant release for 240 h. To produce hydrogels, synthetic polymers are frequently used, but they do not ensure biodegradability; therefore to develop a biodegradable hydrogel pesticide loaded, natural polysaccharides represent a more promising solution. Yayci and coworkers[115] proposed an hydrogel formulation using pectin and bio adhesive peptides, where the biodegradability of the system is ensured by enzyme activity. Pectin is a renewable raw material that can form microgels functionalized with bio adhesive peptides that guarantee efficient binding between the leaves and the microgels. Thanks to the anchor bio adhesive peptides the system self-assembles in an oriented way on the microgels. This process happens in mild conditions and in aqueous solution, without chemical activation needs, and effectively prevent grapevine downy mildew infection using copper as the active component released. The controlled amount of copper released enables pollution reduction.

Hydrogel release can be tuned accordingly to the environment. Sultan and coworkers[116] developed a carboxymethyl cellulose hydrogel modified with polyacrylamide. The pH and salinity influence on swelling have been investigated. At pH 9 swelling ratio reached 1199.58 %, while in a saline the maximum reached was 349.76 %. The cumulative release percentages of urea at pH 9 was 69.12 %, higher compared to the one in saline solution (38.94 %). The release mechanism involves both a diffusion and a biphasic releasing mechanism, consisting of initial burst followed by a slow release. Combined solutions for fertilizer delivery systems are also possible, Dou and coworkers[117] developed a chitosan-montmorillonite nanocomposite microgel. The technique used include chitosan pellets dissolved into water with acetic acid at 60 °C, mixed with montmorillonite (MMT) in the desired weight ratio (2, 6, 10, 14 g/L have been tested) and after NPK fertilizer is added,

N-glutaraldehyde stabilize the system thanks to the chemical cross-linking, strengthening the microgel structure. The total mixture is then frozen at −26 °C, thawed at room temperature, rinsed in ethanol and finally dried in oven at 40 °C overnight. The inexpensive material that composed this microgel, make this formulation suitable to mitigate the effects of overfertilization. To tune the release according to the field condition, Meurer[118] developed a pH responsive microgel for foliar application that exhibit high swelling in acidic conditions.

The system consist in poly(allylamine) microgels modified with different functional groups by reacting the free primary amine present on each unit of the polymer backbone; then post modification is performed with dihydroxybenzoic acid, a chelating agent that enhance binding specific metal ions; to ensure strong binding to the surface, thiol-ene click chemistry is employed using anchor peptides. The scope of this formulation is to fight the iron-deficiency in cucumber, the system effectively increased the chlorophyll content inside confirming the iron ions delivery to the plants.

### 4.6. Microcoatings

Coating is a relevant technique to enhance long release of microscale CRF. Thanks to coatings, it is possible to physical separate the fertilizer from the soil, obtaining either a slow release or a release after the break of the coating.[119,120] Coatings are simpler methods but still effective to enhance controlled release fertilizer properties. Pang and coworkers[120] focused their attention on oil based coatings of poyurethane. Fatty acids are analyzed thanks to their influence to physicochemical properties and functionality. The vegetable oil based polyols were synthesized thanks to ring opening polymerization (ROP) and epoxidation, they directly are used as coatings in series around urea granules as visible in Fig. 8. Linseed oil provides high hydroxyl value and functionality, the resultant coating express good cross-linking density, with 56 days of urea release at 3 % coating percentage. The nitrogen efficiency was increased by 27.5 % compared to conventional urea application. Palm oil application has also been studied, the hydrophobicity is high but still its coating for urea is not ideal.

To achieve slow release behavior coating technique can be performed using graphene oxide sheets. Cheng and coworkers[119] defined the synthesis of these sheets in a reaction performed without water, starting from graphite in an acidic solution with $H_2SO_4$ and $H_3PO_4$, to obtain graphene oxide flakes with a sheet-like layered structure after the final freeze drying. During the 2–4 h analyzed, compared to uncoated pellets, the graphene oxide coatings present significantly lower release of NPK ions, with 43–57 % released compared to the 81.51–85.64 % of the not encapsulated version. Another coating technique for fertilizer include the use of polyurethane and polycaprolactone. Polyurethane is formed thanks to the polymerization of polyols and isocyanates, from oil industry. To reduce its environmental impact Wang and coworkers[121] defined a double mosaic structure with polyurethane synthesized from hogwash oil.

The double mosaic structure consists of an harder segment phase, made by polycaprolactone, and a softer one, made by polyurethane. Water permeability is performed, and compared to the modified polyurethane, water permeability has been reduced by 61.9 %. In addition,

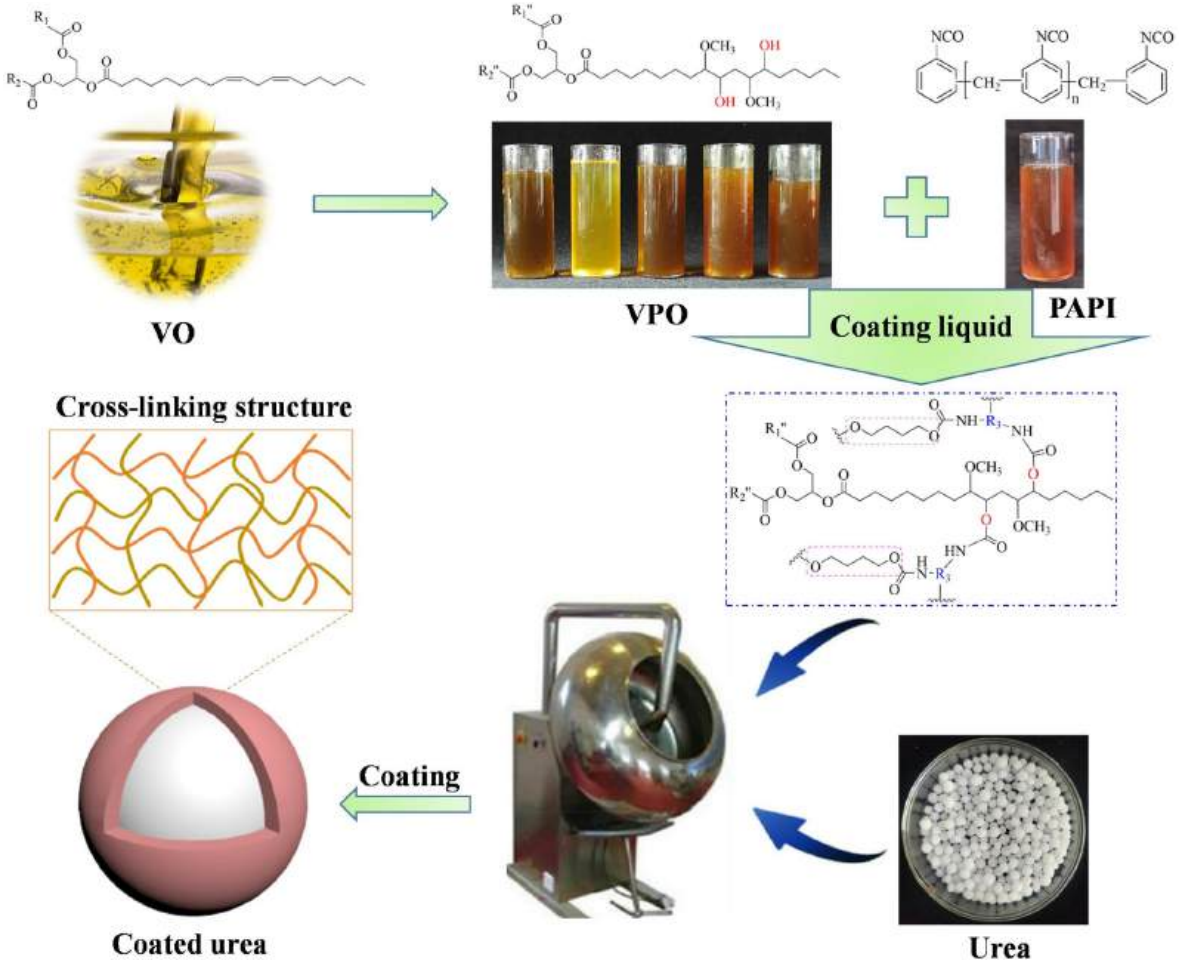


**Fig. 8.** Schematic representation of oil based coatings of polyurethane to produce controlled release systems for urea controlled delivery. Reprinted with permission from MDPI.[120]

hydrophobicity increased by 15.6 %. Cui and coworkers[122] developed a multi-coated slow release system based again on natural rubber natural grafted with poly-acrylic acid. The final structure consists of granules of urea and attapulgite coated with two layers: the first consist of not vulcanized natural rubber, while the second is the grafted natural rubber. N,N-methylenebisacrylamide is used as cross-linking agent for the grafting of natural rubber. The release of N, P and K in a month has also been investigated, resulting in 54.35 ± 1.49 %, 51.18 ± 2.15 % and 44.37 ± 1.38 %, respectively.

### 4.7. Metal compounds

In this section the application of metal compounds in controlled release system is investigated. MOFs and zein use are examples of systems developed. Chen and coworkers[123] developed a CRF for avermectins to enhance its stability to oxidation and photodegradation. MOFs have various advantages, adjustable aperture, remarkable functionality, and adjustable aperture. Due to the toxicity of metal nodes, natural polysaccharide-based MOFs are preferred. Therefore a porous system with gamma cyclodextrin MOFs encapsulating avermectines is developed. The feasibility of a multifunctional platforms for both pesticide delivery and a plant fertilizer have been demonstrated. Loading content of 20.41 % of avermectine is defined, the porosity eases the absorption of the pesticide. From pH point of view, basic medium led to a faster release. In this direction MOFs can be used.[124] The system developed is able to respond to stimulus thanks to the pH-responsiveness, releasing essential oil. The pesticide loading efficiency obtained was of 15.22 %, together with a low photo-degradation (17.99 %) and thanks to the activity against pathogenic fungi, the system maintain was efficient against infections.

## 5. Macrostructures

This section is focused on the structures with a visible dimension, therefore all the solution over 0.5 mm are included. Hydrogel technique is the prevailing one here, but other options such as foams and coatings are included.

### 5.1. Foams

Liquid fertilizer delivery systems using foam as carrier are here investigated. The fertilizer downside consists of their too fast transportation, that bring the fertilizer into soil portions below the roots, causing environmental concerns.[125] Foams application into agronomic practices aims to improve the delivery efficiency to crops thanks to their characteristics such as hydrodynamic stability. Shojaei and coworkers[126] generated foams using a fertilizer solution with urea, ammonium-N and nitrate. The solution is injected with compressed air into a foam generator. The foam-based fertilizer main advantage is the increase of nutrient retention in soil. To control storage of cereal grains and of cereals from organic farming, Germinara and coworkers[127] defined a poly-caprolactone coated structure, with a whey protein foam core, loaded with propionic acid or (E)-e-hexenal. The system is intended to control Sitophilus granarius (L.), a primary pest of stored grains. Both propionic acid and hexenal were able to achieve 100 % mortality after 1 month. However the few literature present on the topic establish that foams cannot be considered as a very promising solution for pesticide and fertilizer controlled delivery due to their extremely low stability and not tolerance to salts and change of pH typical of crop production.

### 5.2. Metal based and complex networks

Finalis and coworkers[128] developed a slow release NPK fertilizer system using biochar and zeolite.

This formulation was used for Allium sepa application, therefore the study wants to support the growth of red onion bulbs. The fertilizer granules are composed by specific mixture of macro-nutrients and micronutrients, respectively NPK and Mg with S.

The biochar was obtained from the gasification of biomass using empty fruit brunches. An alternative use of biochar have been studied by Rubel and coworkers[129] focusing on efficient N delivery. The system does not involve the use of metal compounds but includes inorganic compounds; the proposal includes biosolids, bioasphalt, bentonite, rice starch, besides, and ammonium sulphate. The blend is dried, extruded and cut in particles of 2x2-5 mm. The intended use is within greenhouses. 80 % of nitrogen have been released after 30 h. The leakage of nitrogen has also been reduced.

### 5.3. Pellets, briquettes

The alternatives presented in the previous sections may have complexity as counterside. Adu-Gyamfi and coworkers[130] proposed instead a simpler solution, a fertilizer deep placement technology within the savanna zones in Ghana. This consist into briquette particle placed into the soil, near root zone, with the aim of improving nitrogen plant uptake. It was observed that the best results in terms of nitrogen recovery efficiencies and from gross profit margin point of view, are achieved with 75 % briquette, over than 100 % solution. As mentioned, developing a CRF with biodegradable material is a major advantage. Volova and coworkers[131] developed a formulation with urea embedded in a poly-hydroxyalkanoates matrix. The comparison of different format, films, pellets and polymer coated granules were studied. The structure confirms a gradual leaching of nitrogen lasting for higher time compared to the alternatives present in literature; several dozen days are needed to achieve the complete release of the urea loaded.

### 5.4. Coatings

Respect to the coatings sub-section within nano and micro delivery section, the characteristic dimension of the final system is in the range of a few mm. Fertilizers are here usually presented in granules, which are then coated according to the intended use. Compared to agriculture in calcareous soils can be challenging. Therefore Narayanasamy and coworkers[132] developed a multi-nutrient fertilizer, to provide precise intake of nutrients that plants need to grow. The tested coatings for granules include amino acids and organic acids at different concentration (1 %, 3 %, 5 %, 10 %).

Granules have been prepared using sulfur as fertilizer and micronutrients such as zinc, iron, copper, and boron. To achieve complete granulation a binder is added to the formulation. The organic acids tested and amino acids tested are citric acid, humic acid, fulvic acid, salicylic acid, and glycine. Free $CaCO_3$, pH and nutrient release were monitored during the 45 days of control. The 10 % citric acid solution ends up being the most promising solution for controlled release of nutrients. Other biodegradable polymers are used,[133] lignin extracted from pulp for example is used to develop a three-dimensional cross--linked network, with methylcellulose and citric acid. The fertilizer used are phosphate based. The extraction of lignin from pulp consist in a hot water and alkaline treatment; it is an economic material since it come as waste from paper industry. The coating is formulated using the solution blending method; the matrix is composed of methylcellulose, into which lignin is incorporated, and citric acid is employed as cross-linking agent. The best performances are obtained with high lignin content (40 %). The resulting product is compact, with good barrier property and with enhanced hydrophobicity. Fertahi and coworkers[134] expanded the biopolymer coating on phosphorus with a proposal based on lignin and another on lignin and carrageenan combination. The coating solution with carrageenan alone was excluded due to the high phosphorus release in water. The use of triple superphosphate as fertilizer caused a strong acidification in the soil nearby the granules. The tests were performed into Petri dishes filled with dry soil, hydrated with 31 mL of

distilled water. Non-coated treatment resulted in stronger acidification of the soil; the coated solution showed a larger phosphorous diffusion. An alternative is represented an oil-based hydrophobic system to control the phosphorus release from 3 mm diammonium phosphate granules as proposed by Da Cruz and coworkers.[135] The system is studied into an acid tropical soil. The coating consisting of a castor-oil-based polyurethane resin system was synthesized with dipenylmethan diisocyanate and polyurethane, 40/60 mass ratio. Thicker coating improves the control on phosphor release, since too thin coatings forms irregularity that facilitate the phosphorus release. Bellemjid[136] studied the encapsulation with amidated low methoxy pectins used in a ionotropic gelation within a solution of calcium chloride. To produce hybrid beads, a sol-gel process has been performed, using silica as coating material.

The encapsulated molecule was carbendazim, a common benzimidazole fungicide. The final formulation had a positive effect in reducing the release rate of the fungicide. Higher encapsulation was obtained with not hybridized beads, however the hybrid solution with silica was the one with the slower release rate both in soil and in water. A potassium based fertilizer developed by Legras-Lecarpentier and coworkers[137] was able to prolong the release over 25 days using biodegradable system thanks to technology "enzymes". The fertilizer is based on lignosulfonates that passes through enzymatic polymerization using Trametes hirsuta laccases. This, along with 1 % w/w alginate incorporated, helped having randomly breaking particles of small diameter. The use of lignosulfonate as coating is therefore promising; raising alginate content can further slowdown the release. Lastly, Neto and coworkers[138] developed an urea-controlled release system using carnauba wax and bentonite. Two different encapsulation methods were studied: a mechanochemical method starting with a mixture of granulated urea, natural and sodium bentonite, and a dip coating method that incorporated carnauba wax along with different percentages of bentonite. For the first method urea was prepared both with natural and sodium bentonite, the two powders where separately grinded, mixed and processed. Dip coating technique include, after the preparation of the urea bars, a synthesis of coating solution with bentonite added at different concentration into melted carnauba wax; the bars are then immersed into the coating solution and then dried at room temperature. Soil column test showed the lower urea release rate compared to standard fertilizer.

### 5.5. Hydrogels

Hydrogels, three dimensional networks that are known for their ability of absorbing high amount of water, remaining though insoluble in aqueous solution thanks to chemical or physical cross-linking. This property offers a suitable application for agricultural activity, especially fertilizers thanks to their high hydrophilicity. Hydrogel formulations developed in recent years targeted urea, K, and NPK fertilizer. Mohammadi-Khoo and coworkers[139] synthesized a low cost biodegradable hydrogel, bromoacetylated cellulose cross-linked with urea that can be released over time.

Ahmad and coworkers[140] used cellulose prepared from wastepaper, with epichlorohydrin as cross-linker and carboxy methyl cellulose as gelling agent. They were able to obtain a maximum loading capacity of 0.51 g/g. Different ratio of cellulose fibers was used, favorable performance for the application was obtained with C3 cellulose (3 % w/V cellulose and 1.75 % w/v CMC). With the ideal composition, the maximum swelling capacity of 2000 % was also achieved. Mahfoudhi and Boufi[141] tested at different pH the use of cellulose nanofibrils with poly(acrylic acid co-acrylamide to synthesize a nanocomposite hydrogel. The radical polymerization is reinforced by nanofibrils and methylenebisacrylamide that was used as cross-linker. Nanocellulose decreases swelling capacity but thanks to the polymer chains grafting the compression, the strength can be improved. Higher than 5 % cellule nanofiber (CNF) loading, resulted in a decreased speed of releasing, making it suitable for controlled release application. Tanan and coworkers[142] developed a biodegradable hydrogel, with methylene-bis-acrylamide as cross-linker, grafting copolymerization performed between cassava starch and acrylic acid, and with natural rubber and polyvinyl alcohol tested at different ratios. The final formulation has urea coated with two layers, the inner is the semi interpenetrating polymer network hydrogel, while outside a layer of wax was used.

The natural rubber (NR) NR/PVA ratio 9:1 had the best results with a 38.5 % release at 30 days, Furthermore, the cost of this formulation was 5 times lower compared to the commercial slow release fertilizer (Fig. 9). The production steps started with a rotating drum machine equipped with hot-air gun. Firstly, urea prills were preheated at 70 °C for 10 min. Then 12 g of coating materials (hydrogel solutions) were sprayed slowly onto the surface of urea prills rotated at 35 rpm. The resulting surface was finally coated by wax solution using the rotating drum and labeled as Biodegradable Hydrogels Wax-Coated Urea (BHWCU).

A last option regarding urea is presented by Sarhan and coworkers,[143] chitosan and starch were used as biopolymers with the addiction of microalgae. Maximal urea loaded was between 99 and 440 %, respectively for the microalgae with the starch and the microalgae with chitosan; the urea released was 78–95 % after 30 days. Crucial macronutrient for plants is also studied by Chen and coworkers[144] that fabricated starch-alginate matrix with $CaCl_2$ acting as cross-linker. The best encapsulation efficiency was obtained with high starch alginate concentration and lower KCl content. This is obtained thanks to the more uniform and compact surface. Higher starch-alginate concentration increases also the biodegradability of the final device. Recent studies investigate the development of a specific hydrogel, the superabsorbent hydrogel (SAH), that possess high water capacity. Sousa and coworkers[145] use graft polymerization between babassu mesocarp (babassu is a common palm of south America with high starch content) and polyacrylamide. The addition of potassium phosphate in the hydrogel increases the cross-linking.

Dardeer and coworkers[146] used CMC and polyacrylic acid to develop a different SAH, successfully synthetizing a slow release organic fertilizer for vinasse powder, coated with the SAH to regulate potassium release. The application on field on sugar cane crops prove the applicability of this solution, being able to release for 50 days. Liu and coworkers[147] blended sodium alginate, PVA with the cellulose nanofibers, that benefit the cross-linking activity and the formation of a stable gel. The hydrogel core is stabilized with hydrogen bonds intra and inter molecular, while the outer layer is a IPN shell obtain with chelation and covalent bonding of the matrix with calcium cations. As previously mentioned, cellulose can be extracted from waste paper, Nazeri and Moghadam[148] convert it into CMC that goes through graft copolymerization with acrylic acid and vinyl acetate. Bisacrylamide was used as cross-linker. The hydrogel results sensitive to pH, more basic environment reduces the release rate. As N is the most essential plant, N fertilizer are widely applied, the main source is urea, that is not the only one though. Shanghaleh and coworkers[149] developed a stimuli responsive device able to deliver N fertilizer. Cellulose nanofibers are used from wheat straw, aminated, and combined with a cationic poly acrylate, then the encapsulation was done with ammonium nitrate. The ideal composition among the one tested has 10 mL of acrylamide, 1 mL 2-aminoethyl methacrylate hydrochloride, 0.45 mL aminated cellulose nanofibers, 25 % of N fertilizer ammonium nitrate. The optimal solution was the one with the higher surface area, it shows N release over 90 days in soil cultivated with rice. Zyadeh and coworkers[150] with CMC sodium derived, cellulose, and citric acid as cross-linker, tested two different nitrogen based fertilizers, $KNO_3$ and $(NH_4SO_4)$. The optimal formulation was sensible both to pH and salt, it exhibits 450 % of absorbance capacity and a 1 month durability in deionized water, and a cumulative release rates between 60 and 70 %. Cellulose source can also be bacterial. In this direction Zaharia and coworkers[151] used it to develop IPN hydrogel with poly(acrylic acid-co-N,N′-methylene- bis-acrylamide) that directly encapsulated a liquid fertilizer containing K, P $NH_4$ oxides and

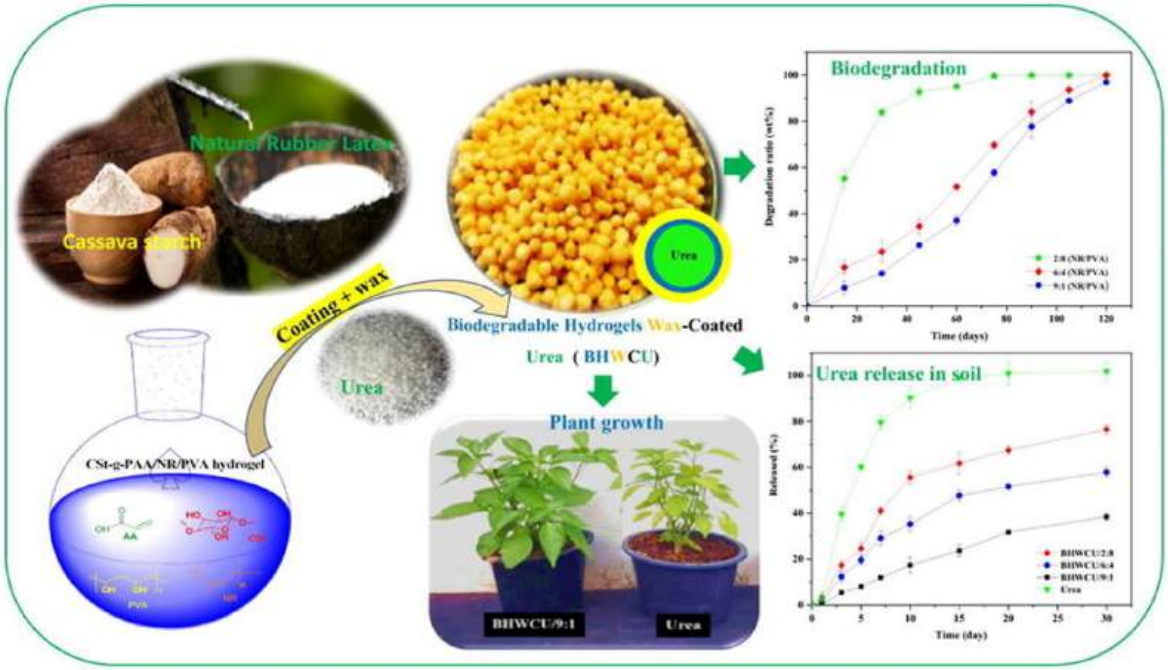


**Fig. 9.** Schematic diagram for the fabrication process of biodegradable hydrogel coated with urea. Reprinted with permission from Elsevier.[142]

micronutrients. Comparison were made between the hydrogel loaded with the liquid fertilizer and one charged with only distilled water. The first one results more stiffed due to the cellulose addiction, therefore thanks to the formation of IPN the fertilizer was slowly released.

As substitute of cellulose cassava starch can be used, Chamoroo and coworkers[152] used it combined with a cross-linker (citric acid) for the controlled release of N and K, under salts form ($NH_4Cl$ and KCl, respectively). Increasing salt concentration decrease both cross-linking efficiency and water absorption content. It was demonstrated that the release mechanism follow Less Fickian diffusion and anomalous diffusion for K and N, respectively. Thanks to this it is possible to state that K release is mainly dependent from water penetration rate, while N depends by the hydrogel mobility. Cross-linking agents, acrylamides and citric acids among all, are of crucial importance, but they can reduce surface area available, and hydrogel property. Pushpamalar and coworkers[153] studied the electron beam effect on a hydrogel to substitute the cross-linking agents. Carboxymethyl sago pulp were used with N fertilizer coming from potassium nitrate and ammonium nitrate. The superabsorbent hydrogel is biodegradable, reaching complete degradation between 3 and 5 months depending on the degree of substitution adopted (directly correlated with the number of pores), but it can be clearly stated that most of $KNO_3$ loaded was released over 50 days. Among the techniques to produce hydrogels, dialysis is a valid alternative, Davidson and coworkers[154] synthesized a root targeted delivery vehicle, by using CMC, and iron and calcium salts to enhance a proper cross-linking. The gel is placed for 48 h in a dialysis membrane, to obtain a ionically cross-linked hydrogel. The vehicle was able to reduce the fertilizer use up to 78 % at fixed plants yield. In addition hybrid organic-inorganic system are continuously attracting interest in different sectors and in particular MOFs combined with hydrogels can take advantages from both systems.[155,156] Guo and coworkers[157] integrate MOFs with nanofibers and sodium alginate to formulate an urea-loaded hydrogel. Loading capacity is 1.47 g/g, while water holding capacity is 63 %. The test on wheat was performed and both germination rate and chlorophyll content doubled compared to the wheat without treatment. Lin and coworkers[155] was able to reach 77.53 % of water retention after 12 h in deionized water, with a cumulative release in soil of 40.84 % on day 30. The hydrogel was based on cellulose nanofibers oxidized with 2,2,6,6 tetramethylpiperidine-1-oxyl (TEMPO).

Nanocellulose oxidized with TEMPO have been also used to develop a pH sensitive solution,[156] with the best performance obtained in an alkaline environment, with 101 g/G water absorption and a water holding capacity upgraded to 51 %. Hybrid inorganic-organic system includes also clays and minerals. Zhou and coworkers[158] provided a suitable application for rice leftover, loading urea as nitrogen source in a network with acrylic acid and montmorillonite metals and rice leftover to deliver N fertilizer. Hydrogen bonding interactions can stabilize the structure, with montmorillonite that impacts on the mechanical strength, resulting in improved water retention capacity and leaching of nitrogen reduced up to 19.7 %. Bauli and coworkers[159] proposed a CMC based hydrogel stabilized with nanoparticles, either nanocellulose, montmorillonite or vermiculite. Less water absorption was caused by higher cross-linking, due to greater interaction between CMC and the filler. Montmorillonite was the one showing the least interactions. The solutions with nanocellulose and montmorillonite were the one potentially applicable for NPK fertilizer delivery. Lastly, Singh and coworkers[160] proposed starch alginate polyacrylamide based hydrogels, focused on a fungicide (Thiophanate-methyl) delivery. The hydrogels absorbed 18.301.40 (g/g of gel) water, making it suitable for arid regions.

## 6. Conclusions and future perspectives

In summary, controlled release systems for fertilizers and pesticides represent alternative tools to ameliorate crop production reducing the drawbacks typical of their use. Despite the extremely promising results found in research studies some concerns should be solved before using these technologies in the place of classic ones. The first obvious one is related to the costs that, considering the field of application, should be very low and comparable with neat fertilizers and pesticides. In addition large scale production is still a problem that should be guaranteed. So controlled release systems have to be optimized and then compared in terms of toxicity, performances, scale of manufacturing, kinetics of degradation and cost-benefit ratio with conventional routes.

In this framework the main issue is represented by the need to assess durability, bioavailability and toxic behavior for the environment in a

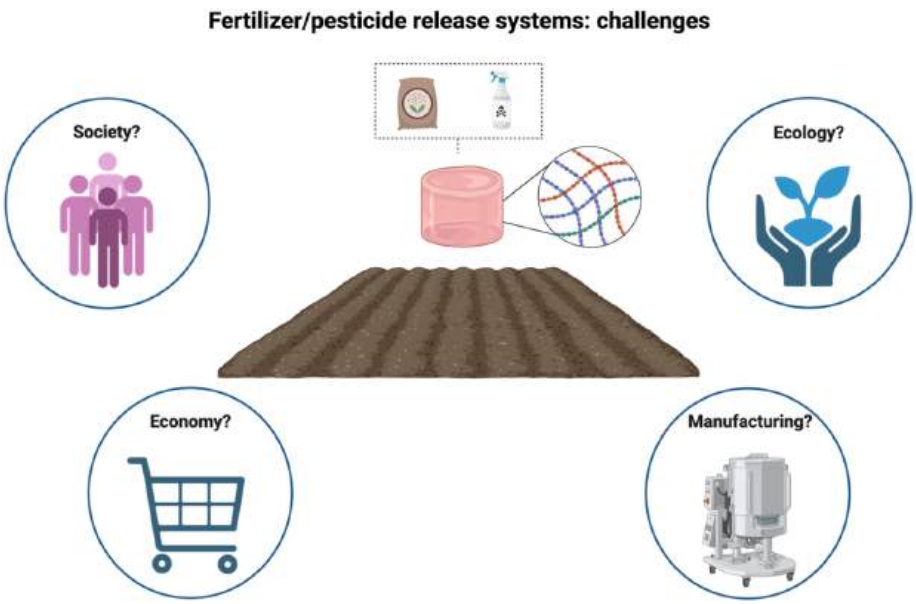


**Fig. 10.** Schematic illustration of design of study for future release systems of fertilizers and pesticides.

reliable way. Indeed the lack of enough data in agriculture field is still a big challenge. A lot of works present toxicity tests while others do not, this calls for the deployment of validated techniques that can generate enough information on delayed toxicity of these devices. Here Safe-by-Design (SbD) approach can help to reach quickly the market (time to market). SbD is a fundamental instrument able to identify uncertainties and risks involved in human health and environmental safety during the initial stages of the device development. During the proper design of polymeric materials the key part is represented by the tailoring of their properties in accordance with their end usage. The materials used as controlled release systems should control and sustain the delivery of their cargo and remain stable during time. Moreover the toxicity tests should involve the couple pesticide/fertilizer-polymer and the neat polymer. What is generally used to evaluate the biological interface interactions and toxicity are:

- (Quantitative) Structure-Activity-Relationship ((Q)SAR): regression analysis historically used for drug discovery. It aims to find a relation between materials properties and the desired activity. The model will give a numerical prediction be able to asses if a certain material is safe for the related application;
- Grouping and Read-Across. It aims to fill data gaps, initially creating groups of materials properties and/or effects and then through interpolation for missing data. Here the idea is that similar materials show similar properties. Such an interpolation allows to predict a certain material endpoint if data are not available;
- Molecular modelling. This technique is a powerful tool to predict the interactions across polymer surfaces and small molecules. It is a complementary tool to lab activities, since it can be used to understand some complex interactions. However, it cannot replace completely lab experiments and it cannot be used as a merely prediction tool.

Moreover an other key element, that need to be further analyzed, is the possible leaching of active molecules from controlled release systems. Many research works underlined that it is one of the main side effects with consequent water and soil pollution.[161–163] The plausible study design for the requirements of controlled release system for fertilizers and pesticide is visible in Fig. 10. In summary, the devices discussed in this review present great potentialities as innovative technology able to overcome the drawbacks of traditional routes. The success in their development can revolutionize the crop production, contributing to global food security. However it is crucial to underline that they can offer a large number of benefits and their use as controlled fertilizer/pesticide delivery must be approached with a deep understanding of potential environmental and human health consequences. Careful considerations and responsible implementations are fundamental to guarantee that controlled release system can positively contribute to agriculture field without harming environment or human well-being. For the future strong attention should be given not only to all the considerations done before but also to different possibilities to develop multi-responsive systems tailored to specific crop-soil environments. There is indeed an increasing evidence that such intensive agroecosystems cause a decline in biodiversity as well as threatening the environment and have damaged a huge number of ecosystem services such as the biogeochemical nutrient cycles and the regulation of climate and water quality.

Consequently, the main challenge that agriculture is facing is to guarantee the future of food production while reducing the use of inputs and limiting the environmental impacts and the loss of biodiversity. This approach can guarantee not only optimal crop production for today but also for the future.

## CRediT authorship contribution statement

**Stefano Di Rago:** Writing – original draft. **Francesco Morandi:** Writing – original draft. **Fabio Pizzetti:** Writing – review & editing, Supervision. **Filippo Rossi:** Writing – review & editing, Supervision, Funding acquisition.

## 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.

## Abbreviations

| | |
|---|---|
| AVM | avermectin |
| CAR | chlorantraniliprole |
| b-CD | b-cyclodextrin |
| CK | cytokinin |

| | |
|---|---|
| CMC | carboxymethyl cellulose |
| CMTKG | carboxymethyl tamardin kernel grum |
| CNF | cellulose nanofiber |
| CO-PU | castor oil base polyurethane |
| CRF | controlled release formulation |
| DA-6 | diethyl aminoethyl hexoanoate |
| DNF | dinotefuran |
| DZ | dazomet |
| EB | emamectin benzoate |
| EO | essential oil |
| FMA | fumeric acid |
| GSH | glutathione |
| I3A | indole-3-acetic acid |
| IPN | interpenetrating network |
| LC | lambda-cyhalothrin |
| LSMM | liquid starch based mulching materials |
| MC | microcapsule |
| MMT | montmorillonite |
| MOFs | metal organic frameworks |
| mPEG | poly(ethylene glycol) methyl ether |
| NCNPs | natural char nanoparticles |
| NPK | nitrogel phosphor potassium |
| NR | natural rubber |
| PDI | polydispersity index |
| PEG | polyethylene glycol |
| PLA | poly-lactic acid |
| PLGA | poly(lactide-co-glycolide) |
| PVA | polyvinyl alcohol |
| PYR | pyrimethanil |
| SAH | superabsorbent hydrogel |
| SRS | slow release systems |
| TEMPO | 2,2,6,6 tetramethylpiperidine-1-oxyl |
| UV | ultraviolet |
| ZIF-8 | zeolitic imidazolate framework |

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