Biobased Materials as Promising Tools for the Slow-Release of Urea

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ABSTRACT: The exponential growth of the world's population in recent years increases the necessity to optimize the technologies associated with the agricultural sector. In this direction, a smart use of fertilizers is able to guarantee high productivity, avoiding problems related to fertilizers losses from volatilization and leaching with consequent pollution issues. An extremely promising solution is represented by slow-release fertilizers (SRFs) that are able to increase the efficiency of fertilizers, lowering their application frequency and preserving the environment but still satisfying the nitrogen requirement of the plants. However, most of the devices used come from non-renewable sources with consequent problems related to environmental pollution. So, in the last years, research efforts moved to materials that present similar release properties but, at the same time, are cheap, environmental friendly and biodegradable. The aim of this Review is to focus on biobased polymeric devices used as slow release systems of urea. In particular, strong attention will be dedicated to different polymers and different formulation strategies in order to understand the high amount of possibilities and performances of these devices.

KEYWORDS: biomaterials, food engineering, polymer, sustainability, transport phenomena

1. INTRODUCTION

Enhancing and optimizing agricultural productivity has been one of the main challenges of the last decades due to the persistent growth of the population and the gradual decrement of arable land.[1] Fertilizers are the fundamental input materials for crop production since they are able to provide the specific nutrients required for the growth of plants. By being the main responsible for increasing the agricultural production and quality of crop yield, their utilization needs to be urgently improved to address global changes. Various fertilizers, particularly nitrogen-based, have been employed in high amounts to enhance crop yields. Nitrogen, indeed, is the most widespread element for soil fertility and is considered the key macronutrient source for crops.[2] Urea fertilizers have become widespread thanks to the high content of nitrogen (46%), good availability and low cost.[3] The amount of urea produced was 179.8 million metric tons in 2022 with an actual cost of 377.5 USD/ton, and it is expected to trade at 360.78 USD/T by the end of 2023. In terms of physical properties, its high soluble characteristics cause significant economic and resource losses as well as environmental pollution.[4] About 40% of the urea is lost through ammonium volatilization, denitrification, and leaching, which consequently leads to an increased usage of fertilizers to compensate for the losses.[5] In particular, urea can be transformed into NH_4, which could then become NO_3 and which can be lost by leaching or volatilization after nitrification. To face these issues, efforts have been made in improving nutrient-use efficiency and make agriculture green and sustainable. In this direction, urea inhibitors are commonly used to reduce the loss of urea due to the pathway described above.[6,7] Another very promising solution is represented by strategies directed to the improvement of fertilizers efficiency, lowering their application

frequency, preservation of the environment but still satisfying the nitrogen requirement of plants,[8,9] commonly known as slow-release fertilizers (SRFs).[10] The main difference between them is that urea inhibitors do not control the amount of fertilizer in the ground but act on only the lifetime of urea. SRFs are commonly prepared by coating or encapsulating conventional fertilizers with different materials, usually water-insoluble or porous. They gradually release nutrients and simultaneously reduce their loss to the environment through water penetration control.[11,12]

Fertilizers, coated onto polymers or encapsulated, can be produced using several types of industrially available coating processes. Good examples are the pan coater, the rotating drum, and the fluidized bed. The use of pans or drums is very widely used due to the low cost of these processes; however, the low coating efficiency and the list of coating materials does not guarantee to deposit onto the granule surfaces a good film. To improve these aspects, the use of the fluidized bed technique is necessary. The kinetics of nutrient release strongly depends on the type of agriculture, ground condition and the environment in terms of temperature, humidity and differences between night and day times. Most of the widely used materials come from petroleum sources and are characterized by non-renewability, and environmental pollution during the release.[13] As a result, the focus has shifted towards biobased materials that exhibit the same release properties as common
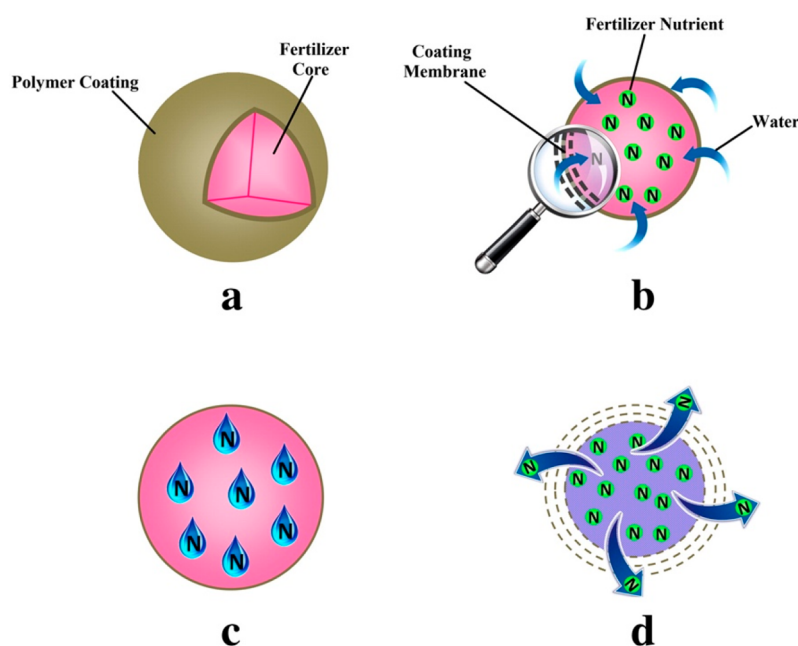
Figure 1. Diffusion mechanism of controlled release: (a) Fertilizer core with polymer coating. (b) Water penetration into the coating and core granule. (c) Fertilizer dissolution and osmotic pressure development. (d) Controlled release of nutrient through swollen coating membrane. Reprinted with permission from ref 9. Copyright 2014 Elsevier.

SRFs but are biodegradable, environmentally friendly, and have low production costs. Indeed their use increased in the last years thanks to the actual need to reduce the emission of potentially hazardous chemicals during device manufacturing and their use. In addition the possibility to use in these devices materials that come from agricultural residues reduces the costs and help to close the loop of circular economy related to this field.[14,15]. There are mainly two types of alternative SFRs: matrix-type formulations and coated systems. In the first, the nutrients are dispersed in a matrix and diffusion occurs through the pores of the carrier phase. They are widely employed due to ease of production. The latter instead are more similar to conventional SFRs in which a fertilizer core is surrounded by additional materials, and the nutrient release occurs through a shell.[16,17] Both are suitable for formulations with organic-based products and still exhibit release capabilities consistent with conventional systems. This Review aims at describing the use of innovative natural polymer-based carriers for the slow release of urea, the most widespread and used fertilizer. Indeed, we will focus our attention not only on applications but also on the materials characterization and in particular on fundamental properties for the release systems such as water retention capacity, swelling and adsorption/desorption.

As said, the use of biobased materials is very promising and for the first time is highlighted in a Review paper to discuss where the research is and where it can go. For this purpose, the most investigated property is the urea release profile as it relates to its implementation in possible practical situations.

2. MECHANISM OF FERTILIZER SLOW RELEASE

It is critical to understand the controlled release mechanism since is the direct measure of an SRF's effectiveness. The controlled release mechanism is dependent on many factors like the type of fertilizer, the nature of the coating material and the agronomic conditions. Several possible mechanisms are

described in the literature with both many similarities and differences between them.

The multi-stage diffusion model was proposed by Liu[18] and Shaviv[19] as a release mechanism for coated fertilizers. After applying the coated fertilizer, water enters within the coating able to condense on the core of the solid fertilizer with consequent partial nutrient dissolution. As osmotic pressure builds within the containment, the core granule starts to swell, resulting in two processes. The first is called "failure mechanism" or "catastrophic release". This takes place when osmotic pressure exceeds the specific threshold of membrane resistance, causing the coating to burst, and the entire core is spontaneously and rapidly released. Instead, the second process is known as the "diffusion mechanism", and it occurs when the membrane can resist the increasing pressure. The core fertilizer is thought to be slowly released via diffusion, with the driving force being a concentration or pressure gradient, or a combination of the two. Nutrient release by diffusion can be described by three main moments: lag phase, steady release phase, and decay phase[20] Water, mainly in vapor form, reaches the fertilizer core during the lag phase where the driving force is the vapor pressure gradient, and the release has not yet started. It follows a linear phase of constant nutrient release by equilibrating this gradient. Finally, the decay phase is reached in which the release slows down steadily, and the inner core is found to have a decreased nutrient concentration as the release was almost complete in the previous phase.

Frail coatings (e.g., sulfur or modified sulfur) are more likely to exhibit the failure mechanism, whereas polymer coatings are more likely to exhibit the diffusion release mechanism. Figure 1 depicts a schematic representation of both mechanisms. The rate of nutrient release is also affected by soil temperature and moisture content. The rate of release increases with increasing temperature and moisture content.[21] The coated fertilizer release mechanism can be described as a nutrient transfer driven by water, either coming from irrigation or rainfall, from

the fertilizer—polymer interface to the polymer—soil interface. Diffusion/swelling, polymer coating degradation, and dissolution are the governing parameters for the release from materials.

3. SLOW-RELEASE DEVICES

Although the application of slow-release fertilizers is already being employed to reduce the environmental impact caused by ordinary fertilizers, these are usually synthesized from non-renewable sources and otherwise cause harm to the environment in which they are placed.

For this reason, current research is increasingly moving toward replacing all non-biodegradable materials with environmentally friendly alternatives such as biopolymers, either natural or synthetic, and blends formed from renewable or waste resources. Examples of synthetic degradable polymers are polylactic acid (PLA), polyvinyl alcohol (PVA), polydopamine (PDA), and derived from natural resources like poly(3-hydroxybutyrate) (PHB). They were already proposed as valuable options in the development of polymeric coatings for SFRs.[22,23] Chen et al.[24] proved that the starch-g-poly(L-lactide) (PLLA) could be used for urea coating urea to delay its nutrient release. As an alternative, different raw natural biomaterials have been used such as starch, cellulose, lignin, chitin, and other polysaccharides. However, these cannot be used directly but must undergo both chemical and physical modifications to improve their properties especially those related to the release of compounds.[25−27] These materials are therefore used to make systems suitable for the fertilizer loading and subsequent release, which is why they are combined with specific formulations thought for this purpose. Innovative systems of SFRs can be summarized in the following formulations:

- Hydrogels;
- Aerogels;
- Nanomaterials: nanogels, nanocomposites, nanofibers.

3.1. Hydrogels. Hydrogels are defined as cross-linked hydrophilic polymers able to absorb a large amount of water and aqueous solutions due to the presence of hydrophilic functional groups.[28,29] The presence of crosslinks in their three-dimensional structure preserves the stability of swollen hydrogels and prevents them from dissolution. The resulting physical entanglement and chemical grafting enables to simultaneously absorb and retain water and additional compounds loaded even under external pressure.[30−32] Given their excellent water-absorbing capacity, they can be used in the agrochemical field as an efficient water management tool.[33]

They allow to improve soil quality by acting on its water retention capacity,[34] promote the formation of soil aggregates that enhance its structure,[35] improve soil aeration while mitigating its degradation, reduce water evaporation losses, and extend nutrient retention in soil. The application of a hydrogel as a fertilizer carrier thus ensures two simultaneous mechanisms, the release of nutrients into the soil and the preservation of its water capacity. However, most of the conventional hydrogels are characterized by poor mechanical strength, which has limited their application in various fields.[36] As a result, several methods are used to enhance these properties and make hydrogels suitable carriers. Among these, two commonly used techniques are creating a double network structure and incorporating inorganic nanomaterials into the hydrogel.[37−39] Most of the hydrogels are made from synthetic

hydrophilic polymers such as poly(acrylic acid) and poly-(acrylamide),[40] but the rising demand for biocompatible, biodegradable, non-toxic alternatives has led to the use of polysaccharides such as starch,[35] cellulose,[41] chitosan,[42] and alginate,[43] as carriers for fertilizers. They contain the same hydrophilic functional groups which can be modified by cross-linking and copolymerization to be used in the preparation of hydrogels.[44−46]

3.2. Aerogels. Aerogels are solid structures characterized by their extremely lightweight nature and porosity that can reach up to 99.9 % (v/v). These materials are created through drying wet gels, during which the liquid present in the pores is replaced by gas[47]. Aerogels are extremely tunable nanomaterials due to their capability of possessing pores ranging from macro (>50 nm) to micro-scale (<2 nm),[48] along with high specific surface area which makes them suitable to be used as carriers[49]. Depending on the nature of the materials employed in the production of the gel structure, aerogels can be either inorganic or organic.[50] The first category involves sources as silica, metals, oxides, and chalcogens, while the second focuses on polymers of both synthetic and biobased nature.

Biopolymers such as chitosan, alginate, pectin, lignin, and cellulose, have already been successfully used for the preparation of aerogels mainly for biomedical applications, such as tissue engineering and drug delivery systems.[51] Given their aptitude for the controlled release of molecules, they have also been studied with an application in the agrochemical field.

3.3. Nanomaterials. Nanotechnology collaboration with agricultural and food science is emerging as a potential approach to increasing plant growth and yield.[52] Owing to their peculiar characteristics as their small size and shape with high surface area, nanomaterials have become viable options for the slow delivery of nutrients. Using nanomaterials as SRFs has the potential to decrease the use of chemical fertilizers while maintaining or even increasing agricultural production.[53,54] The main advantage of these materials lies in the great versatility of formulations that can be obtained such as nanogels,[55] amphiphilic polymers,[56] nano clay-polymer composites,[57], carbon nanotubes,[58] carbon nanofibers.[59] All these different carriers, together with polymers of synthetic or natural origin, can represent the matrix phase in the preparation of nanocomposites.[60] Composites are multiphasic heterogeneous solid materials where the matrix phase is continuous while the reinforced phases are not.[61] Nanocomposites, in particular, are a unique type of composite in which nanomaterials with at least one dimension up to 100 nm are added to the matrix.[62] This size reduction allows the nanocomposites to behave differently and be characterized by a large surface area to volume ratio. Several synthesis procedures can be implemented according to the desired end formulation: graft solution polymerization,[63] ion-exchange method,[64], free radical polymerization,[65] and in situ free radical polymerization.[14] Most of the nanocomposites that can be employed as nutrient delivery for plants can be divided into three main classes:

- Nanomineral-based nanocomposites;
- Polymeric nanocomposites;
- Porous carbon-based nanocomposites.

A representation of several types of nanocomposites with a possible application as fertilizers is reported in Figure 2.

The most common example of nanomineral-based nanocomposites is represented by nanoclays. These can be defined
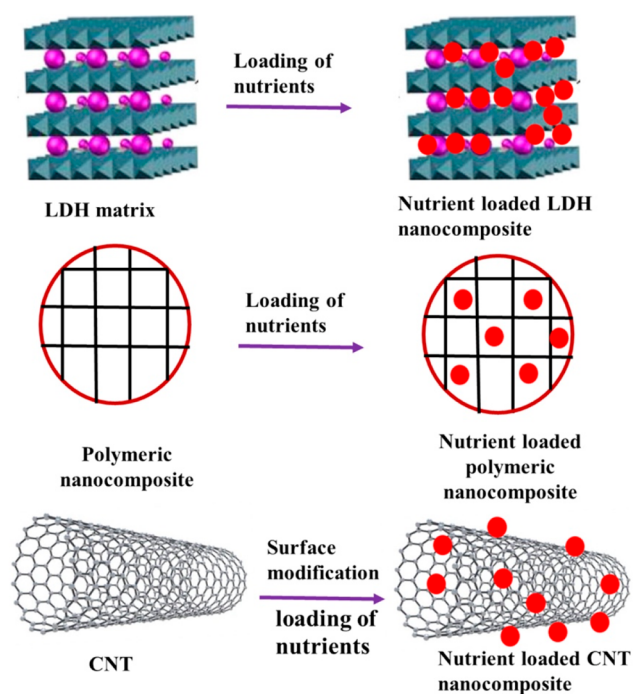
Figure 2. Representative examples of different types of nanocomposite-based fertilizers. Reprinted with permission from ref 20. Copyright 2023 Elsevier.

as bi-dimensional layered mineral silicate nanoparticles with enhanced mechanical properties that allow them to safeguard nutrient molecules both through physical barriers and their intercalation into the layers of nanoclay minerals due to ion exchange and non-electrostatic interactions. Nanomineral-based fertilizers can be obtained either by the employment of nano-sized clay minerals as the matrix for compound entrapment or by using them as reinforcement of polymeric matrix that will function as a nutrient confinement system. Nanoclays can be either anionic (e.g., layered double hydroxides (LDHs)) or cationic (e.g., nano-sized montmorillonite and nano-zeolite). Nano-sized montmorillonite has been used to produce a slow-release urea nanocomposite fertilizer.

This was achieved by intercalating nanoclay and urea, resulting in a slow-release behavior even at low concentrations of nano-montmorillonite (20% w/w)[10] with a loading capacity

of 6%. On the other hand, zeolite was employed as a nano-N fertilizer (referred to as nanozeourea) applied to maize and managed to regulate N availability for up to 45−49 days. It was able to lead to a noteworthy increase in total nutrient content, plant growth, quality, and yield.[66] Another type of nano-composites is polymeric nanocomposites, in which the continuous phase is a polymer, while the reinforcing phase is a material with at least one dimension up to 100 nm.[67] They can be synthesized with different techniques as solution processing, filler intercalation followed by in situ polymerization, and melt intercalation.[62] The porosity of nano-carbon composites is the feature that allows them to also have a high surface area, which makes them excellent adsorbents.[68] Carbon-based nanomaterials including nanofibers and nano-tubes can be loaded with metals such as iron, zinc, and copper that represent micronutrients necessary for crop growth. For this reason, they can be used as growth promoters by guaranteeing and enhancing nutrient delivery and at the same time also regulating water absorption.[69,70]

4. POLYMERS FOR UREA CONTROLLED RELEASE

4.1. Cellulose. Cellulose is a polysaccharide that consists in a linear chain of β-1,4 D-glucose units that is the main structural component of plant cell walls. It is tasteless, odorless, and insoluble in water and most organic solvents. It is an hydrophilic material with high inter and intramolecular hydrogen bonds and van der Waals forces that prevent it from dissolution.[71] Being the most abundant natural material, it can be obtained from several renewable materials as cotton,[72] wheat straw,[4] hemp, and other plant-based materials.[73] Mainly due to dissolution complexity, its application can be limited. To widen its employment, cellulose can undergo several chemical reactions to obtain different derivatives according to specific needs. Examples of the most spread derivatives are hydroxypropyl methylcellulose (HPMC), hydroxyethyl cellulose (HEC), and carboxymethyl cellulose (CMC).[74]

Mohammadi-Khoo et al. were able to develop an eco-friendly hydrogel system based entirely on cellulose able to load 17% of urea.[41] To enhance the release mechanism, it was first bromoacetylated (BA) and then crosslinked with urea to form the required hydrogel (Figure 3). Both water-holding (WH) and water-retention capacity (WR) were investigated on soil samples containing different amounts of hydrogel and both results showed that WH and WR capacities increased by increasing the hydrogel content. For instance, the WR
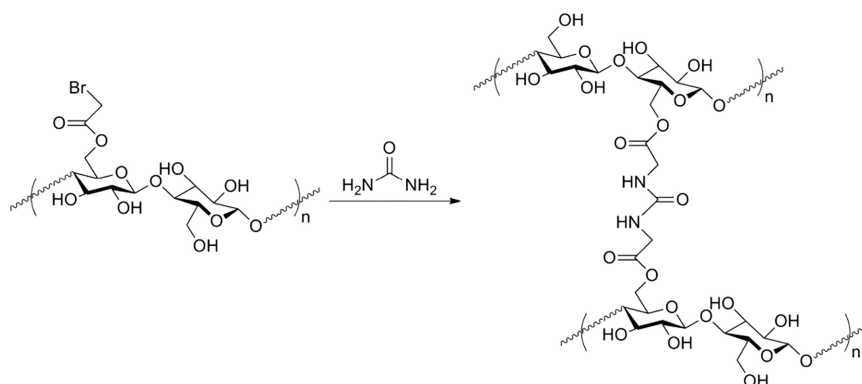
Figure 3. Crosslinking of BA cellulose with urea. Reprinted with permission from ref 41. Copyright 2016 Wiley.
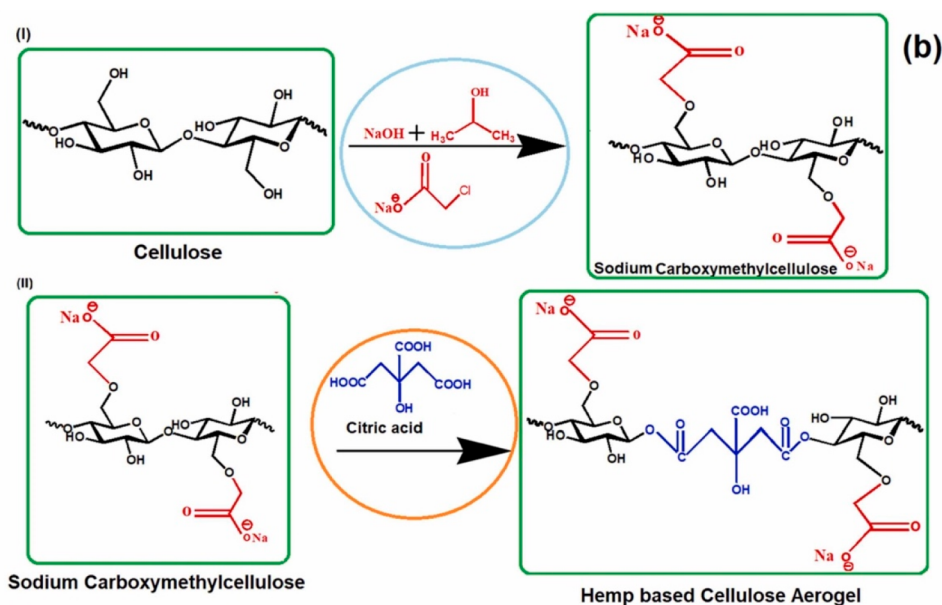
Figure 4. Steps of cellulose conversion. Reprinted with permission from ref 82. Copyright 2023 Elsevier.

capacities after 15 days of testing were 7.85% for pure soil while 16.85%, 19.98%, and 32.75% for 0.5, 1, and 2% samples, respectively. In the case of neat urea, the release is almost instantaneous and complete in a few minutes. Consequently, agricultural lands with these moisture-holding additives could store a lot more water during irrigation or rainy seasons and gradually release it during periods of drought.

Guo et al.[32] formulated a cellulose composite hydrogel, taking advantage of its excellent slow water retention capabilities but decided to combine it with the presence of metal-organic frameworks (MOFs). These are non-toxic, biodegradable, highly structured, porous materials characterized by large specific surface areas, unsaturated metal sites, and tunable nanoscale pore structures.[75,76]

The combination of MOFs with hydrogels has been extensively studied in cancer treatment,[77,78] as drug release systems because the high surface areas they are provided with show excellent suitability for drug loading and releasing. In addition, burst drug leakages is limited by the three-dimensional network of the hydrogel itself. Therefore, due to the resemblance of the drug release mechanism with the slow release of nutrients for agrochemical purposes, the employment of MOFs and hydrogels has been extended as urea carriers. As MOF, MIL-100(Fe), a transition-metal MOF with a rigid zeotype crystal structure, was chosen for its additional nontoxicity and environmentally friendly characteristics.[79] Cellulose nanofibers (CNFs) synthesized from eucalyptus pulp[80] were used since they show a larger specific surface area and smaller volume with respect to ordinary cellulose. Urea was loaded aftyer material production into the hydrogel in a very high amount of 1.47 g/g. This was possible due to the pronounced porosity of the structure, which therefore facilitated its absorption. Equally positively, its release into the soil then occurred. In 15 days, about 45% of the urea present was released, reaching up to 60% at 30 days while for the uncoated fertilizer more than 85% was released by the second day, and on the fifth day, the amount of the released content had reached 90%. From the results obtained, it is possible to confirm that when the hydrogel is placed underground, it begins to adsorb water and gradually swells

due to the abundance of carboxyl groups. With increasing hydrogel volume, the three-dimensional network structure of the hydrogel expands. As a result of the dynamic exchange of free water, it enters the interior of the hydrogel, and urea molecules slowly diffuse out of the network pores. The internal tortuous paths of the hydrogels imparted by MIL-100(Fe) can slow the overall urea release. The extension of the hydrogel network begins to slow down, corresponding to hydrogel saturation, resulting in a reduction in urea molecule release. Senna and Botaro[81] studied a hydrogel made from cellulose acetate crosslinked ethylenediaminetetraacetic dianhydride (HEDTA) by esterification crosslinking and loading with NPK (ammonium, phosphate, and potassium) fertilizer.

The HEDTA was able to reduce the leaching of NPK fertilizer compared to commercial fertilizer: 1.9% of ammonium, 1.6% of phosphate, and 8.5% of potassium were leached out from HEDTA instead of 1.7%, 80%, and 98%, respectively, in the commercial system.[81] A different approach focused on the circular economy, was adopted by Kaur et al.[82] An innovative eco-friendly aerogel was produced employing waste hemp stalk-derived cellulose with an urea loading capacity of 19.51%. To prepare the aerogel, cellulose was first converted to carboxymethyl cellulose (CMC) via sodium monochloroacetate initiated esterification and then further cross-linked using citric acid (CA) to a yield the typical three-dimensional structure of aerogels (Figure 4). CMC consists of a cellulose backbone with glucopyranose repeating units with carboxymethyl groups attached to at least one hydroxyl group of cellulose. Unlike cellulose, it is soluble in water due to the presence of ionic carboxymethyl groups which enable molecules to hydrate.[83] Also in this case, swelling behavior and fertilizer release mechanism in water and soil were investigated. The aerogel absorbed 80 g/g water after 27 h at neutral pH, showing super-absorbent behavior due to its highly porous structure (>90%), large free volume available amid polymeric chains, high presence of hydrophilic groups, and high specific surface area (200-600 m^2/g).[49] It also displayed a sustained release of the chosen encapsulated nutrients namely urea and ammonium dihydrogen phosphate (ADP). For urea, the percentage of a mass release of nutrients in water after 40 h

was 48.4%, while in soil it was 62.28% after 120 h, which demonstrates that it is highly suitable for improving soil quality. In the case of neat urea, the release is almost instantaneous and complete in a few minutes in water, while this occurs in less than one day in a soil environment.

4.2. Starch.
Starch is the most widely employed polysaccharide owing to its multiple applications in the food industry as a thickener, stabilizer, and gelling agent. Its popularity relies on its low cost, ability to replace synthetic polymers, suitability to chemical modifications, renewability and biodegradability.[12,84] Starch granules are microparticles with both crystalline and amorphous regions mainly composed of amylose and amylopectin.[85] Amylose has a linear structure made of glucopyranose units bonded via α-D-(1−4) glycosidic bonds. Amylopectin, on the other hand, is characterized by a branched structure, where the linear branches are combined through α-D-(1−4) glycosidic bonds and periodically combined through α-D-(1−6) glycosidic bonds.[86] It has emerged as a valuable option for the preparation of hydrogels due to its eco-friendly features and its ability to absorb large amounts of water.[87] However, its employment is limited by hydrophilicity but also low viscosity and brittle nature due to strong interactions between starch macromolecules that limit polymeric mobility.[88] To satisfy and comply with the requirements of hydrogels, especially as SRFs, different modification strategies can be resourceful to change their physicochemical properties.

A common technique is the esterification modification in which the hydroxyl group of a starch is converted to the ester group through dehydration.[89] In this way, it is obtained an esterified matrix with enhanced hydrophilicity, viscosity, and plasticity that can be exploited for the preparation of SRFs.[90] This was achieved in the work by Dong et al.[27] They studied a starch phosphate carbamate hydrogel (SPC-Hydrogel) and its corresponding urea hydrogel (SPCU-Hydrogel) as slow-release fertilizer (Figure 5), prepared by a one-step free radical
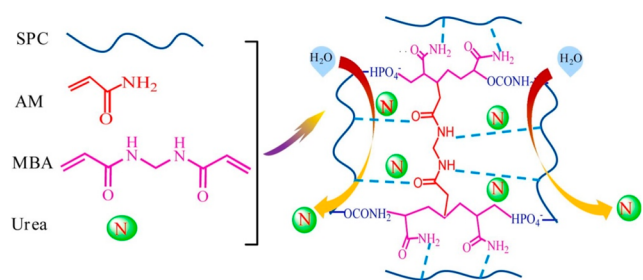
Figure 5. Schematic illustration of the chemical structure of SPCU-Hydrogel and release mechanism. Reprinted with permission from ref 27. Copyright 2021 Elsevier.

copolymerization of SPC and acrylamide (AM) without and with urea addition. Both release tests in water and soil were performed (loading capacity equal to 19%). Compared with pure urea and native starch-based urea hydrogel (NSU-Hydrogel), the SPCU-Hydrogel released 50.3% in 15 h, achieving an almost complete release in about 25 h in water. In the case of neat urea, the release is almost instantaneous and complete in a few minutes. In soil testing instead, the complete release of urea was reached after about 35 days. They also performed tests on maize seedlings to intuitively assess whether the presence of the SPCU-Hydrogel favored plant growth. Comparing a sample in plain soil, one in neat urea-

based soil, and one with the SPCU-Hydrogel, it was found an increase in the number of leaves (4 for plain soil, 5 for neat urea and 5 with SPCU-HG) and stalk size in terms of length (8 mm for plain soil, 12 mm for neat urea and 16 mm with SPCU-HG) and width (3 mm for plain soil, 3.2 mm for neat urea and 4.3 mm with SPCU-HG),.

An alternative to esterification is represented by graft polymerization. With the modification of grafting monomers, different changes in properties can be obtained. By graft copolymerization with vinyl acetate, starch-g-poly(vinyl acetate) (St-g-PVAc) can be obtained. It shows a core−shell structure with the core of hydrophilic starch but the shell of hydrophobic PVAc grafts. This membrane was proposed for the encapsulation of urea by Niu and Li.[91] The release rate of urea decreases with increasing graft efficiency of PVAc on starch. When the graft efficiency of St-g-PVAc reaches 47%, the urea in St-g-PVAc composite films showed excellent slow-release behavior: the urea release did not exceed 15 wt % by the second day, and about 78 wt % of the urea was released after 30 days. In the case of neat urea, the release is very quick and complete in less than 15 hours in a soil environment. These results confirmed the slow-release properties of these composite films by comparing them to the standard of slow-release fertilizers proposed by the Committee of European Normalization (CEN).[92] Moreover, after 60 days of exposure in soil, the composites appeared fragile and decreased by 56% in the size that indicates the spontaneous degradation of these films in the soil environment. Another example of modified starch as a coating system is shown in the work by Tanan and coworkers.[93] Biodegradable semi-interpenetrating polymer network (semi-IPN) hydrogels of cassava starch (CSt)-g-polyacrylic acid (PAA)/natural rubber (NR)/ polyvinyl alcohol (PVA) were prepared as coating membranes for SRFs. The hydrogel wax-coated urea (BHWCU) was obtained by coating urea particles with the semi-IPN hydrogel and wax. Results showed that higher NR/PVA ratios caused a significant decrease in water swelling, modulus, water retention, and biodegradation of the hydrogels. Among the formulations proposed, the BHWCU/9:1 one exhibited an excellent slow release of nitrogen in both water (47.5% at 168 h) and soil (38.5% at 30 days), relating also to the lowest surface area (1.95 m^2/g) and pore volume (3.75×10^{-3} cm^3/g). In the case of neat urea, the release is almost instantaneous and complete in few minutes in water, while the release occurs in less than one day in a soil environment. Gungula et al. were able to propose starch-based hydrogels by encapsulating urea into biopolymers and using borax as a binder.[94]

The peculiarity of this solution, however, is that the biopolymers employed are derived from plant-based sources namely *Borassus aethiopum* (BA) and *Maesposis eminii* (ME). Both BAS-SRF and ME-SRF showed similar effects on the water retention behavior of the soil. The water retention ratio of the soil with SRFs at 4 days was about 14.76%, whereas without SRF, it was 4.67%, implying that both can enhance the water retention capacity of soil and therefore improve the ability of draught resistance of the plants. Cumulative release rates of urea encapsulated in BAS-SRF and ME-SRF in water and soil were also determined. The released rate of pure urea in soil reached 96% in 3 days. While sustained and controlled released behavior was observed for the SRF-hydrogels. At 10 days only about 24% and 29% of the urea in BAS-SRF and ME-SRF were released respectively. The maximum was observed at 36 days where about 94% and 92% of the urea
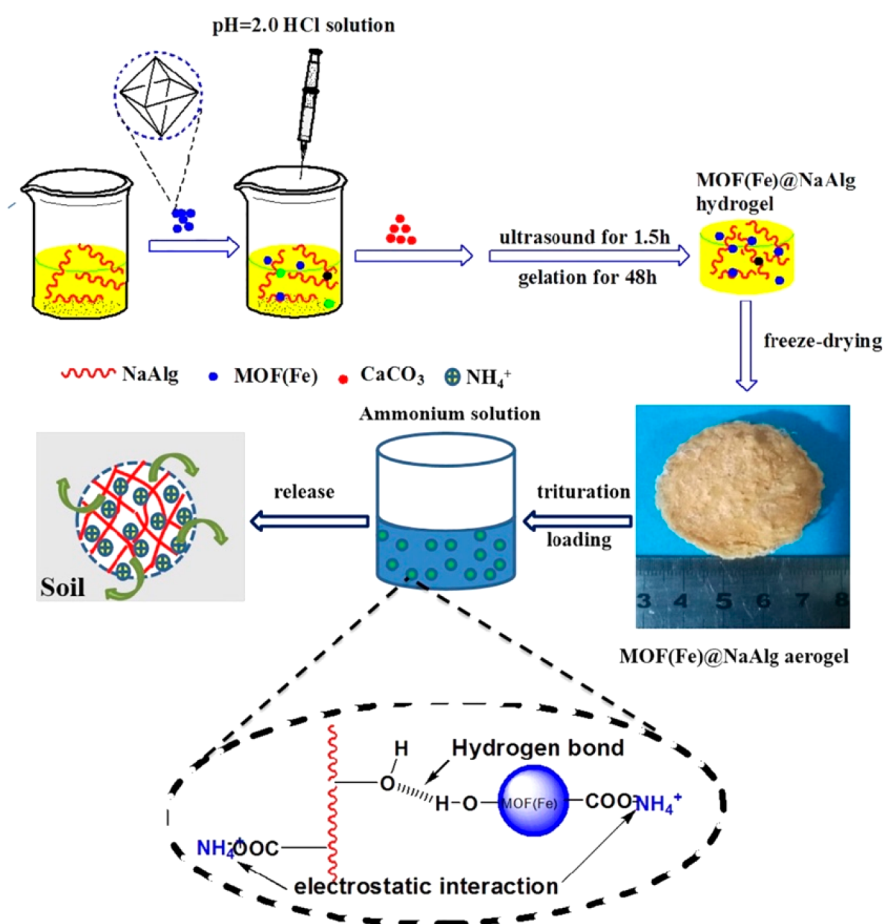
Figure 6. Proposed pathway for preparation, adsorption, and release of MOF(Fe)@NaAlg composite aerogel. Reprinted with permission from ref 49. Copyright 2020 Elsevier.
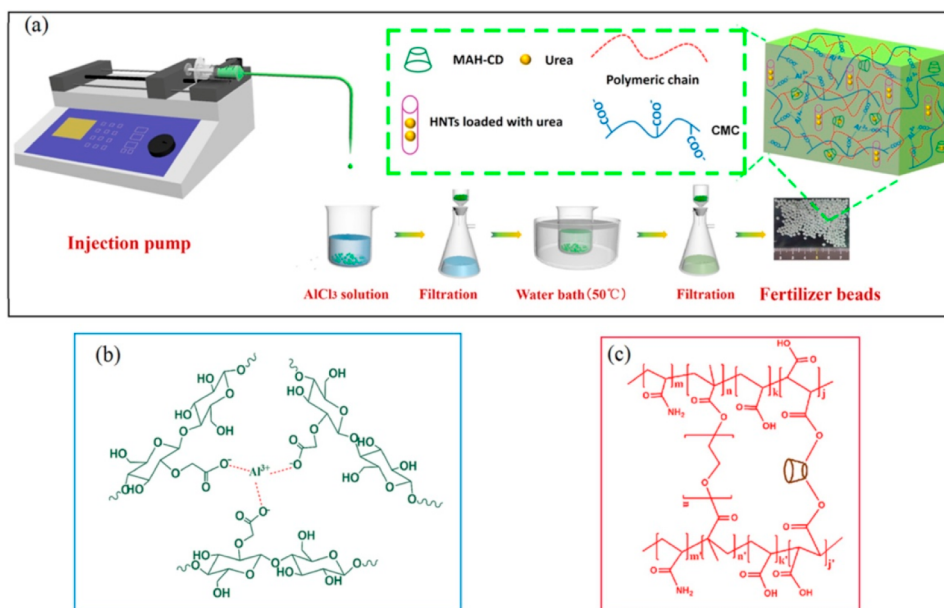
Figure 7. (a) Preparation procedure and schematic illustration of the structure of the WSF. (b) Physical structure of the network formed by ionic crosslinking. (c) Chemical structure of the network formed by free radical polymerization. Reprinted with permission from ref 99. Copyright 2021 Elsevier.

encapsulated as BAS-SRF and ME-SRF respectively were released.

4.3. Alginate. Alginate is a linear polysaccharide derived from seaweed, composed of alternating units of α-1,4-L-

guluronic acid and β-1,4-D-manurunic acid units. It is biodegradable and has excellent water-holding properties, making it useful in various applications such as food, pharmaceuticals, and biotechnology.[95] It can be obtained from bacterial sources, but usually, it is available from algae in the form of salt, in particular as sodium or calcium alginate.[96] Sodium alginate (NaAlg) is able to form stable metal-biopolymer composites with multivalent metal ions (Ca^{2+}, Fe^{3+}, Al^{3+}) through crosslinking interaction since it is characterized by multiple hydroxyl and carboxyl groups on its structure.[97,98] As a result, NaAlg-based formulations represent an ideal green organic matrix to immobilize particles by forming porous, open, three-dimensional structures, as proved by Wu et al.[49] They studied the possibility to have a NaAlg-based aerogel as a high-performance slow-release N-fertilizer (Figure 6). To improve the adsorption capacity, MOFs were employed. In this case, an iron-based MOF was obtained by hydro-thermal method from ferric chloride ($FeCl_3 \cdot 6H_2O$).

The aerogel was prepared to adsorb ammonium from water and then release N both in water and soil. The sample with (2:10) mass ratio of MOF(Fe) and NaAlg showed the highest swelling capacity of 73 g/g and in its release tests, the cumulative N release in soil reached 70% after a month of testing.[49] Its release behavior is consistent with the nature of the diffusion mechanism in aerogels and complies with the standard of slow-release fertilizers of the Committee of European Normalization (CEN).[92] Shen et al.[99] proposed a double network fertilizer obtained via the ionic crosslinking of sodium alginate and $CaCl_2$ and the free radical polymerization of β-cyclodextrin (MAH-CD), in an aqueous solution of urea, in which halloysite loaded with urea was pre-suspended.

Figure 7a shows a schematic representation of the preparation procedure, and both the physical and chemical structure of the network are reported. Double network hydrogels show enhanced mechanical properties if compared to single network hydrogels, such as high toughness, high failure resistance, and high-water content. One of the most widely used techniques for creating double-network hydrogels is the employed ionic crosslinking, which is frequently accomplished by incorporating multivalent cations in the matrix. Halloysite is a cost-effective, biocompatible nanoclay that was added to adjust the swelling behavior and the slow release of urea.[100] In particular, halloysite nanotubes (HNTs), were employed. These are naturally occurring aluminosilicates with hollow tubular structures that have inner and outer diameters of 10−30 nm and 40−70 nm, respectively, with many surface-active groups that make them excellent reinforcements for polymers.[101] Water retaining and urea slow-release experiments were performed and showed that the presence of HNTs increased both the water-retaining ability of soil and the release time of urea to 95.2% in five days of testing compared to 98.7% of the SRFs not containing HNTs.

A similar purpose is achieved in the work by do Nascimento et al.,[102] in which they still propose alginate-based hydrogels but decided to use cellulose nanocrystals (CNCs) as a reinforcing agent, enhancer of mechanical properties and swelling ratio. CNCs are highly crystalline water-dispersible derivatives of cellulose that were prepared by acid hydrolysis from cotton linter fibers, They were incorporated into the gelatin hydrogel and then an external alginate membrane was applied to the inner one. When compared to a plain gelatin hydrogel, the compressive modulus of the hydrogel with 5.0 wt % CNCs was enhanced by 288 % and also showed both better slow-release properties and water retention and also a staider control of the possible burst effect.[103]

4.4. Chitosan. Chitosan (CS) is a linear polysaccharide obtained from partially deacetylating chitin, one of the most available natural polysaccharides found in the shells of crustaceans. It is a polycationic polymer that consists of N-acetyl-D-glucosamine and D-glucosamine linked by β-1,4 glycosidic bonds and is characterized by several free amino and hydroxyl groups that make it suitable for structural modifications.[104] It is biodegradable, biocompatible, and shows antimicrobial properties.[105] Chitosan is naturally insoluble in water, but multiple strategies can be used to increase its solubility such as quaternization using glycidyl tri-methyl-ammonium chloride (GTMAC) and methyl iodide.[106] Through a reaction with GTMAC, it is possible to synthesize a water-soluble derivative N-(2-hydroxy-3-trimethylammonium) propyl chitosan chloride (HTACC) that turns out to have superior antimicrobial activity, adsorption capacity, moisture retentiveness, and permeation enhancing property with respect to chitosan.[107,108] Arafa et al. proposed to synthesize a hydrogel for the controlled release of urea by cross-linking alginate and HTACC.[42] The synthesized hydrogels exerted significant antimicrobial activities and molecular docking showed their binding affinity toward glucosamine-6-phosphate synthase, β-lactamase II, TraR binding site and nucleoside diphosphate kinase.

Urea loading onto Alg/HTACC hydrogels depended on the swelling degree of hydrogels, so the maximum loading percentages of samples AH1 (50% Alg:50% HTACC), AH2 (60% Alg:40% HTACC), and AH3(70% Alg:30% HTACC) at 5 M urea concentration were 107%, 112%, and 200%, respectively. Sodium alginate was added because of the hydroxyl and carboxyl groups on its backbone that favor the cross-linking with the positive charges of HTACC in an aqueous solution.[67] This organic system aimed at efficiently retaining water, and releasing urea in a controlled way, but also preventing the growth of pathogenic microbes by modulating metabolic enzymes, thus exploiting the antimicrobial activity of chitosan. The results showed that the maximum urea loading could go from 107 to 200% and its release rate reached the equilibrium condition between day 28 and day 30 with a cumulative amount of about 80%. Jayanudin et al. instead proposed the employment of CS as microspheres for carrier material for the controlled release of urea.[109] The formulation is based on an emulsion obtained by using glutaraldehyde saturated toluene (GST) as the cross-linking agent. The urea loaded was absorbed in the cross-linked matrix, between the amine group of chitosan and the aldehyde group of GST. The nitrogen release was studied, and it began with the chitosan microsphere absorbing water. The highest value of cumulative release reached 37.69% after 30 days. The combination between CS and glutaraldehyde as cross-linker has also been explored by Vo et al.[110] Their main point was to improve the water absorbency and mechanical performance imparted by chitosan by blending it with poly (vinyl alcohol) (PVA). They both are biodegradable and present functional groups that can react with different reagents to change the structure of hydrogels for controlled release applications. In situ hydrogelation was performed by forming a cross-link between CS and PVA molecules by a glutaraldehyde agent in the presence of urea, targeting the fine dispersion of urea into the hydrogels. Samples characterization showed possible interactions based

on hydrogen bonding between urea molecules and polymer functional groups. A high degree of cross-linking produced a dense cross-linking structure, and high hydrolytic stability but a lower urea release concentration. Instead, higher urea content reduced the cross-linking degree but increased the urea release rate over 10 days in distilled water with no burst release in the initial stage.

4.5. Other Biomaterials. Hydroxyapatite is a crystalline, thermostable, and biodegradable mineral, widely employed in bone tissue engineering and dental repairs.[111,112] A particular application is a nanoscale-sized hydroxyapatite which has already been investigated as a source of phosphorus fertilizer. Sharma et al.[113] reported the synthesis of zinc and magnesium-doped hydroxyapatite-urea nanohybrids for slow release and delivery of nitrogen applied to wheat and rice crops. They slowly released nitrogen for up to six weeks, reaching a cumulative release of 40%, as opposed to the usual burst release of nitrogen from urea. When applied to wheat crops, they enhanced crop yield by 22.13% and nitrogen uptake by up to 58.30%. The nanohybrids remained in the soil for two continuous crop cycles and proved to reduce ammonia volatilization by 36% compared to an ordinary control treatment. In the case of neat urea the release is almost instantaneous and complete in few minutes in water while in less than one day in soil environment. Furthermore, soil dehydrogenase activity and urease activity indicated that the nanohybrids had no negative impact on soil microorganisms. The decision to modify the nanoparticles by doping them with metal ions, specifically zinc, and magnesium, was motivated by the positive effect their presence has on the surface area, which they improve by modulating the size and shape of the particles.[112,113] Elhassani et al. developed novel composite materials based on coated urea with calcium phosphate encapsulated woodchip species for use as nitrogen-loaded slow-release fertilizers.[2] SRFs based on woodchips are becoming more and more popular because they are both biodegradable and compatible with soil composition. As the plant decomposes, the woodchip can act also as an organic fertilizer, increasing the organic matter content in the soil.[114] The basic fertilizer was urea-supported calcium phosphate while the wood-based coating was sugarcane bagasse (*Saccharum officinarum L.*) and its derivatives such as lignin and cellulose. The outcomes suggested that immobilization of urea on HA particles leads to an effective SRF owing to the strong interfacial interactions found between amine functions of the urea and carbonyl groups located on the surface of HA.

Water immersion experiments revealed that the urea-modified HAP encapsulated by sugarcane bagasse, cellulose, and lignin composite had a slower and more sustained nitrogen release than the urea-modified HAP over 60 days.

5. FUTURE PERSPECTIVES

As a result of the reported applications and studies, it can be stated that using biomaterials as the basis for slow-release urea systems is surely possible and would combine improved agricultural performance with the increasingly important issue of sustainability. However, some aspects need to be addressed and that could determine the future development of these technologies. First, the interaction of these systems and the materials employed with crops, animals, and human beings following their release at different trophic levels, possible co-contamination with other soil pollutants, and toxicity to non-target organisms should be investigated. Toxicity testing and risk assessment should be conducted about the possible accumulation of substances in the food chain, given their application as fertilizers, and what their accumulation in the environment might entail. Another aspect to be considered concerns the study of their efficacy and performance in real field situations under usual conditions, including atmospheric, to be able to obtain realistic information also by assessing directly crop growth. Following application in a realistic environment, the release mechanisms should be investigated further, evaluating release patterns to compare them with the theoretical models obtained from controlled experimental trials. Moreover, strong attention should be given to their stability during time, avoiding aggregation and agglomeration. In agriculture this is peculiar because the temperature and field conditions are very different, depending on day or night, summer or winter and regional uses. Finally, the cost impact associated with the implementation of these systems should also be assessed, especially on a larger scale. As they are also designed for cost-effective green synthesis, this is a feature that should be preserved but could be compromised in the case of large-scale commercialization.

The factors that could influence costs include both the raw materials required but also possible scale-up-related process costs. Therefore, both optimization of the usage of biomaterials and the accurate definition of easily scalable and implementable production processes are required. In particular strong attention should be given not only to the choice of the material but also to the technique used to manufacture them. This in order to allow the production of fertilizers with higher performances respect to neat urea and so able to compensate the higher costs. Details on economic consideration can be read in the manuscript written by Mansouri and co-workers.[115] In summary, the research community is in strong agreement with the fact that controlled release-based materials present better performances respect to classic products but the actual high cost make their use possible only in specific situations. But in the next years, national or international laws can limit the use of urea, and so an engineering solution, like the use of these devices, could finally obtain an extraordinary economic success.

6. CONCLUSIONS

Fertilizer use in agriculture is critical for satisfying the rising global food demand. However, relevant environmental and health issues have been identified in the post-green revolution era caused by improper fertilizer use, which has resulted in increased greenhouse gas emissions, eutrophication, and groundwater contamination among others. The application of fertilizers able to be released slowly is one of the possible means for limiting the damage caused by the inevitable required use of fertilizers. Indeed, these systems provide the same performance as traditional fertilizers but at the same time, they are able to safeguard the environment. An even more effective option is to synthesize them with biomaterials and biopolymers. In this way, the biodegradable, biocompatible, and low-cost nature of many promising materials is exploited to make slow-release systems with proven efficacy and, above all, environmentally safe. Various formulations compatible with this purpose such as hydrogels, aerogels, and nanomaterials have been proposed.

All these formulations have been widely proven to be effective in the release of substances, and their suitability for urea release has been pointed out in this Review. The great

versatility of these systems is also reflected in the possibility of producing them with different types of biomaterials reported such as cellulose, alginate, chitosan, starch, and others. The above-listed studies reveal very promising results, especially employing the same materials and the different morphologies studied are optimized to improve the fertilizer release mechanism. In the future, the possibility of applying more biomaterials for the same purpose is expected but focusing on the study of the behavior and performance of these environmentally friendly systems not only at the experimental level but in the open field, to obtain realistic and concrete results by evaluating the effect on plant growth and the surrounding environment.

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Notes

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