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Review Article

Controlled and Prolonged Release Systems of Urea from Micro- and Nanomaterials as an Alternative for Developing a Sustainable Agriculture: A Review

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The world population requires the increase of food products from agricultural fields and also the improvement of agricultural practices to avoid the environmental pollution. Urea is the most used fertilizer worldwide; however, it is lost to the environment by processes such as leaching, volatilization, and denitrification. As an alternative to avoid these losses, controlled-release fertilizer (CRF) and prolonged release fertilizer (PRF) have been proposed. With this type of system, the plants could take the necessary amount of nutrients for their growth at the same time decreasing the environmental pollution. These systems could be fabricated from both synthetic and natural sources, such as wheat gluten proteins, polysaccharides, and composites (polymeric matrix, wheat-gluten-urea mix, among others). This review gives a sustainable agriculture approach in the application of CRF and PRF using inorganic and organic raw materials, focusing on the use of wheat gluten proteins and urea for the development of these systems.

1. Introduction

Nowadays, it is estimated that, by 2050, the use of urea in agricultural crops will increase around 130 to 150 millions of tons per year [1]. The urea is the main nitrogen fertilizer used worldwide due to its high nitrogen content (46%) that helps to increase yield and quality of the agricultural products [2, 3]. However, 40% to 90% of the urea applied to the agricultural soil is lost to the environment causing pollution issues, such as soil acidification, soil hardening, and water contamination, and also, it can affect the farmers' economy due to low-quality products and undesired yields [4–6].

The nitrogen losses are carried out through three processes; (1) denitrification, (2) volatilization, and (3) leaching [7–9]. These processes are involved in the biogeochemical urea cycle, where the urea is transformed to ammonium carbonate. Then, the ammonification process is performed to obtain ammonium which can be absorbed by the plants [7, 10]. The ammonium that is not absorbed is transformed to nitrites and then to nitrates through a nitrification process, where the latter is a highly assimilable form by the plants [7]. However, the ammonium and the nitrates formed during the cycle that is not fully absorbed by the plants are transformed in different nitrogen forms such as ammonia, nitrous oxide, and molecular nitrogen under several soil conditions [7, 10]. In the leaching process, the nitrates get lost through the soil until they reach the groundwater, which means that the environmental pollution is not the only issue with this process: human health is also affected [7, 11].

The denitrification process consists of an anaerobic reduction of nitrates to nitrites through the intervention of enzymes, microorganisms, and favorable conditions for this process in the agricultural soil, such as lower oxygen concentrations, which causes the loss of N towards the environment [10, 12]. The volatilization of ammonia represents a serious environment issue since the ammonia can return to the soil in two ways; (1) mixed with the rain that is named wet deposit, and (2) attached to the solid particles around the atmosphere that is called dry deposition [7, 12]. This pollutant is one of the causes of the eutrophication and acidification of the ecosystems. Leaching and volatilization of ammonia are the most important processes to consider in the nitrogen loss into the atmosphere and groundwater [7, 10, 11, 13].

In the last decade, researchers have been working on the development of systems that could effectively provide nutrients to the crops and, at the same time, avoid a high loss of the nitrogen into the environment. Recently, studies have been focused on the development of urea-coating materials, such as sulfur-coated urea, sulfur polymer-coated urea, polymer matrix-coated urea, and starch-based polymer-coated urea [14]. Also, other studies have been focused on the super absorbent/water retaining coating materials and biocomposite-based coating materials [10]. Urea coating materials present several issues, such as high sensitivity to soil properties, light, and heat [14]. Furthermore, urea coating materials are highly expensive and some of them present weak coating barriers [14].

Nowadays, the researchers have been focusing on the study of biopolymers to develop release systems. At this point, wheat-gluten proteins have been used for the development of systems that could have potential applications for urea release systems in agricultural fields. Castro-Enríquez et al. [15] developed wheat gluten membranes loaded with urea and demonstrated their potential application as a prolonged-release system of urea based on the lab results. Barreras-Urbina et al. [16] propose the study of wheat gluten proteins for the development of nanoparticles with potential application in agricultural fields.

Several organic and inorganic materials have been studied for the development of the prolonged-release fertilizers, such as resins, starch, and proteins [10]. Wheat gluten is a polymeric network that is environmentally friendly and can be easily obtained. This material not only has applications in the food industries but also in the agriculture industries. In this review, we discuss the properties, advantages, and disadvantages of the application of several CRF and PRF. Likewise, the possible use of a biopolymer as wheat gluten with potential application as prolonged-release system of urea in agricultural fields will be discussed.

2. Fertilizers

2.1. Natural and Synthetic Fertilizers. Fertilization is one of the main factors influencing the yield quality of agricultural products [17]. The natural (organic) fertilizers are very heterogeneous compounds, and their characteristics or contribution of nutrients can vary according to their origin and the way to process and apply them [18]. Natural and synthetic fertilizers are used even in combination to avoid dependence of agricultural fields on synthetic fertilizers only [19]. The advantages of the application of natural fertilizers are that they can help to increase the enzymatic activity and the soil respiration and increase the biomass of the soil [20]. Other contributions are that organic fertilizers could increase the carbon content, make the soil structure stable, and reduce the N and P losses [21, 22].

However, natural fertilizers also have disadvantages: (1) the nutrient content is low, so it requires large volumes to meet the needs of the plant, and (2) the release of nutrients is carried out very slowly, which could contribute to the plant being affected by a scarcity of nutrients [18, 21, 23]. The most common natural fertilizer is compost, which is an aerobic transformation of natural compounds to organic matter that can be used as fertilizer for agricultural crops without damaging the growth of plants [24]. Also, the compost is considered as the best method for the treatment of natural secondary compounds for their transformation into organic matter with fertilizer application [24].

There is also a variant of the compost, which is called vermicompost, in which organic matter passes through the intestine of the worm taking advantage of its metabolism to increase bacterial enzymatic activity and obtain a stable compound as a final product [24]. The natural (organic) fertilizers are not applied at large scales for agricultural production; they are used in small crops and gardens, while synthetic fertilizers are the most widely used in the world.

On the other hand, the use of inorganic (chemical) fertilizers can lead to agricultural soil deterioration and environmental pollution [25]. However, their use is preferred because of the advantages that they present, such as the easy solubility in water and, through this process, the plants capture the nutrients in a direct and fast way. In addition, the contribution of nutrients is high compared to natural fertilizers so plants can meet their needs with small quantities [18, 23].

In the agricultural fields, the nitrogen is the primary nutrient to develop food from agricultural crops. Likewise, this makes it a limiting factor for agricultural production [26, 27]. Industries have been producing large quantities of nitrogen fertilizers, such as ammonium sulfate, ammonium nitrate, NPK (nitrogen, phosphorus, and potassium), and urea, mainly [27–30]. However, the most used fertilizer worldwide nowadays is urea due to its high nitrogen content (46%), high solubility, easy application, and its easy production (Figure 1) [6, 26, 29, 31]. Urea is manufactured through a heterogeneous reaction that results in dehydrated urea, which is marketed as granular urea or conventional urea by the agrochemical industries [30, 32, 33].

Nevertheless, the application of synthetic fertilizers, as urea, might result in the nutrient not being fully utilized and the nitrogen being lost into the environment through physicochemical processes [12]. The urea loss into the environment could reach around 90% of the fertilizer through processes, such as volatilization, leaching, and denitrification [34].

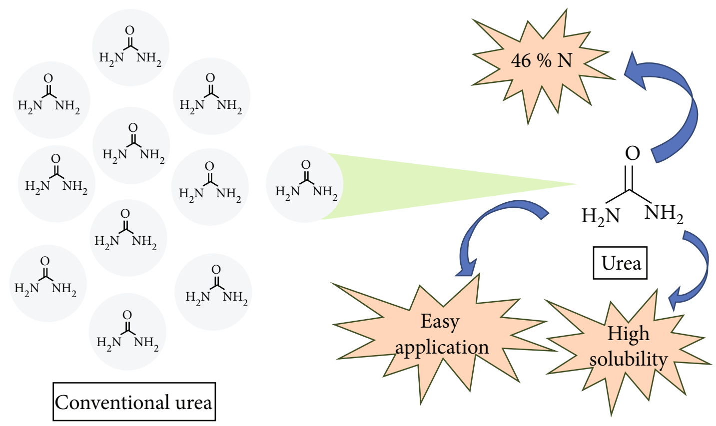

Figure 1: Scheme of the conventional urea and its advantages.

It is known that the fertilization process is the main factor that limits the agricultural production worldwide. The researches have been focused on the development of new fertilization practices where plants can take advantage of the entire nutrient and decrease or prevent losses into the environment.

3. Functionality and Raw Materials for the Development of Controlled and Prolonged Release Systems

The use of materials obtained from different sources for the preparation and development of controlled or prolonged-release systems has been studied in recent decades. Since the current fertilization practices are not very friendly with the environment, the scientists have the objective to improve the agricultural practices. Furthermore, these agricultural strategies are not very effective for the plant nutrition [35], e.g., the efficiency of the main nutrients for the plants, such as *N*, *P*, and *K*, is around 30 to 35%, 18 to 20%, and 35 to 40%, respectively, of the total nutrient applied [36].

The materials for the preparation of these systems have to present several chemical and physical properties depending on the source and the future application, i.e., the material must have low solubility in water with a barrier function for the easy dissolution of the nutrients [35]. That is, the material can present hydrophobic parts in its structure to avoid the rapid dissolution of the nutrient that is interacting chemically or physically with the protective matrix. The nutrient release is given by the dissolution of the urea in water, which is caused by the irrigations in agricultural fields. The release of urea is controlled by the diffusion process or matrix degradation-diffusion process, which could possibly be carried out at the same time [35].

Urea release systems can be developed using nanotechnology which produces particles that are ranging from 1 nm to 100 nm to be considered nanoparticles, while microparticles are in the micrometer scale [37, 38]. In addition, since the physical and chemical characteristics of these composites could be similar, their production would be a suitable alternative for the development of these systems.

However, the development of these systems can be carried out without the use of expensive or complicated technologies, i.e., the materials can be developed in a fast, easy, and economical way depending on the application and the type of raw material. The application of a polymeric barrier could reduce or set a control of the nutrient release and maintain the release behavior. For this reason, the use of natural raw materials, such as polylactic acid (PLA) and poly (lactic-co-glycolic acid) (PLGA), has been widely studied for the development of release systems due to their environment-friendly properties, such as biocompatibility and biodegradability [39, 40]. It is necessary to develop novel materials from other natural sources, e.g., agricultural waste and by-products from the agri-food industries, to give them an extra value and try to make the best use of the waste that is currently generated.

Recently, polysaccharides, such as starch, have been studied for the fabrication of materials with potential applications in agriculture. The starch shows advantages for the development of materials for several industries, e.g., pharmaceutic, agri-food, and medical, such as biocompatibility, environmental friendliness, abundance, and the accessibility to find them in large quantities [40].

On the other hand, materials from natural sources, such as cellulose, hemicellulose, and lignin, can be obtained from the biomass as it is one of the most abundant natural sources worldwide [41]. However, lignin has some issues, e.g., the pure lignin obtention involves the use of aggressive solvents and low yields. Hence, its application as raw material for the development of materials at nano and microscale has been limited. The main advantage of the lignin is that it can be obtained from biomass, which is present worldwide as an agricultural waste. Also, it is a renewable source of aromatic structures that can be found around the world in an inexpensive and very accessible way [41].

Nowadays, research of animal and plant proteins has caught the attention of researchers with the aim to use them for the development of materials. Proteins, such as zein (maize), gliadin and glutenin (wheat), albumin, caseins, gelatin, fibroin, and whey protein, have been used for the production of nano- and micromaterials with potential applications as delivery systems (Table 1) [16, 37, 42]. These

Table 1: Prolonged and controlled release systems.

Materials	Active agent	Application	Release time	Encapsulation efficiency	Morphology	References
Wheat gluten	Diltiazem hydrochloride	Drug release	10 days and 8 days with the mix with PEG	72.8% for wheat gluten and 96.7% for the mix of wheat gluten and PEG 95/05	Spheres	[44]
Gelatin	Fluorescein isothiocyanate dextran (FITC-D)	Drug load and delivery	144 hours	86.4% for FITC-D of 4 kDa and 93.3 for FITC-D of 20 kDa	Smooth spheres	[45]
Chitosan/casein	Chloramphenicol	Drug release	25 hours	Not reported	Spheres	[46]
Silk fibroin	Indomethacin	Drug release	Over 2 days	10.23%	Smooth spheres	[47]
Wheat gluten	Fish oil	Fish oil stability	120 minutes	81.8%	Spheres	[48]
Zein	Essential oils (thymol and carvacrol)	Antioxidant and antrimicrobial activity	Specific time is not reported	More than 50%	Spheres	[49]
Albumin	Therapeutic agents	Drug release	Specific time is not reported	Not reported	Not reported	[50]
Casein	Heat-sensitive or/and acid-sensitive compounds	Freezing stability	Not reported	Not reported	Spheres	[51]
Zein	Thymol	Antimicrobial agent	Not reported	Over 80%	Spheres	[52]
Whey protein	Curcumin	Drug release	48 hours	88.3–96.34%	Spheres	[53]
Wheat glutenins	Urea	Controlled release fertilizers	12 hours	88%	Spheres	[34]
Wheat gluten	Urea	Prolonged-release fertilizer	8 hours	97%	Porous structure (pastille)	[33]

biopolymers present the potential to be considered raw material for the production of release systems that can be used in some industries, e.g., food or pharmaceutical industries [43].

These biopolymers can be obtained as coproducts or byproducts from the agri-food industries [54]. Also, in some cases, the application of these materials involves low environmental and human health risks due to their biocompatibility and biodegradability. Several researchers developed materials with potential application as a controlled release system. Hu and McClements [55] developed particles based on zein-alginate complex with mean diameter size from 50 to 100 nm to produce a release system of bioactive molecules with a potential application in the food and pharmaceutical industries. The authors concluded that the materials formed have a potential application as a natural release system of biomolecules in the food and pharmaceutical areas. Other authors have studied proteins for the development of particles to encapsulate biomolecules. Joye et al. [56] encapsulated resveratrol in biopolymer-based particles to study the effect of the particles under several environmental factors. The authors concluded that biopolymers, such as gliadins and zein, could encapsulate resveratrol for the potential application in commercial food products.

Moreover, some reviews, such as Elzoghby et al. [57], Elzoghby et al. [50], and Joye and McClements [58], show the use of natural compounds as controlled and prolonged release systems in different areas. Also, Barreras-Urbina et al. [16] propose the use of biopolymers as prolonged-release systems of fertilizer using a nanoprecipitation technique. The authors found that the wheat-gluten proteins as gliadins are appropriate for the fabrication of release systems in agricultural fields. It is suggested that the release behavior of these systems should be suitable to satisfy the plants necessities of nutrients. We can realize the importance of the use of materials from natural sources regardless of the application. Yet, the urea loss issues in agricultural fields require alternatives to increase the nitrogen efficiency in plants and improve the agronomic practices.

On the other hand, some inorganic raw materials could be applied in the production of materials at nanometric and micrometric scales. Rodríguez-Félix et al. [59] developed through a green synthesis silver nanoparticles from safflower aqueous extract. The authors tested the antimicrobial activity using *Staphylococcus aureus* and *Pseudomonas fluorescens* and found that the silver nanoparticles have a potential application as antimicrobial agents in the agri-food industries. However, the application of these materials is limited due to its inorganic nature. That is, the material is not biodegradable, environmentally friendly, cheap to obtain, nor fully available. Several inorganic materials that can be used to produce the release systems are, e.g., TiO_2, Ag, Au, ZnO, Cu, and carbon nanotubes [60]. Also, zeolites, ceramics, and silica are inorganic raw materials for the development of nano and microparticles [38].

The raw materials used in the development of nano and microparticles are the main factor to determine their potential application. At the same time, the technique used for the development of materials must be consistent with the nature of the raw material. Currently, it is important to reduce environmental damage and try to develop green technologies or procedures. Also, the development of the release systems from raw materials, which are compatible and friendly to the environment and, in turn, try to avoid or reduce the contamination during production, could make a difference in the agronomic practices and the products obtained.

4. Controlled Release Fertilizers and Prolonged Release Fertilizers

One of the alternatives that are currently investigated to improve agricultural fertilization is undoubtedly the development of controlled-release fertilizers (CRFs) or prolonged-release fertilizers (PRFs). CRFs and PRFs are those in which the nutrient is liberated in a controlled, slow, or delayed way towards the plant, and these systems favor the plant nutritional needs of agricultural crops with a single application [29, 31]. Systems as the CRFs and PRFs present release mechanisms, such as simple diffusion, degradation, or erosion of the polymeric matrix, which helps to release the nutrient from within the system to the outside of the polymeric matrix. The fertilizer, such as urea, can be encapsulated only in the center of the matrix or be mixed throughout the polymer matrix, which would influence the diffusion process (Figure 2) [35].

The difference between a controlled-release fertilizer and a slow or prolonged-release fertilizer is based mainly on the conditions and release behavior. In a slow or prolonged release fertilizer, the release pattern is unknown accurately, i.e., the release rates are inconsistent, and they may be unpredictable to agricultural factors, such as the soil type, weather conditions, and the general conditions of the agricultural crops [29, 31]. The release behavior will depend on the raw material nature, the physicochemical characteristics of the polymeric matrix, and the relation between the polymeric matrix and the fertilizer [61].

Several researchers have focused on the development of this type of fertilizers. He et al. [62] developed a slow-release nitrogen fertilizer with water absorption capacity. A chemical copolymerization was used to develop a gel in which the nitrogen fertilizer was combined with a super absorbent polymer. The authors concluded that the gel behaved as a slow-release fertilizer and, at the same time, it had the water retention capacity due to the hydrophilic chemical groups and the structure of the system. However, it is necessary to continue improving the material.

Considering the importance of fertilization and water in agricultural production, Ni et al. [63] prepared a slow-release fertilizer with the capacity of water retention. Since the main constraints of agricultural production are fertilization and water, the aim of the researchers was to develop a fertilizer capable of delaying the release of N to the plant and retain water. The slow-release fertilizer was developed using ethylcellulose and a crosslinker as poly (acrylic acid-co-acrylamide) (P (AA-co-AM)), and it showed a nitrogen content of around 21.1% and the capacity of water retention that was 70 times over its original weight. The authors

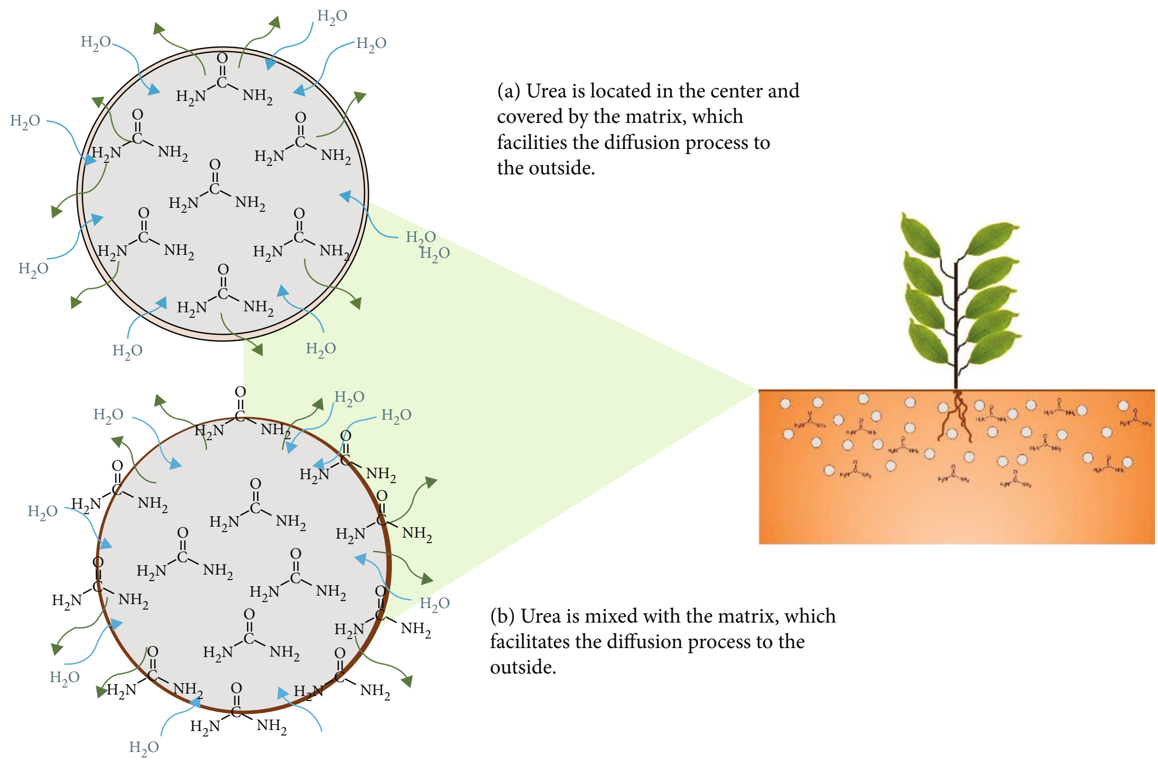

FIGURE 2: Urea release: (a) urea located in the center and (b) urea mixed with the polymer matrix.

concluded that the system can be used as a slow-release fertilizer in agriculture and horticulture.

However, research on controlled release fertilizers has focused not only on a single nutrient but also on the development of controlled-release fertilizers that are capable of absorbing water and releasing nutrients effectively. Zhong et al. [64] developed a super absorbent polymer with an agricultural application based on sulphonated maize starch and polyacrylic acid which contained the phosphate rock fertilizer. The authors tested the release of K and P nutrients where the developed system greatly improved the prolonged release of P and presented excellent water retention capacity. Zhong et al. [64] concluded that the system could be considered for application in agricultural crops based on its prolonged release of nutrient and water retention capacity.

Recently, a study was developed by Qiao et al. [65], where the authors developed a double layer slow-release fertilizer based on ethylcellulose as the inner layer, while the outer layer was composed of a super absorbent polymer based on starch. The authors demonstrated experimentally that there is a difference in the release of fertilizer depending on the source of the starch used for the development of the material. The starch of the potato showed a better release in comparison with starch from different sources. Therefore, through this study, it was shown that superabsorbent polymers based on starch from different sources have potential as nutrient release systems for plants. The authors mention that more research should be done on the structure of the system, focusing on improving the relation of the superabsorbent polymer with the release rates of the nutrient to make the fertilizer release slower and more controlled.

On the other hand, the development of these systems for agricultural and environmental improvement has occurred according to the current needs. The climatic change caused by global warming due to the high degree of pollution has provoked a great interest worldwide to reduce environmental pollution caused by the agricultural industry, specifically in these applications. PRFs and CRFs can help to reduce the use of conventional fertilizers [66]. In addition, adequate dosage of nutrients would benefit not only the production obtaining higher yields but also the plant taking advantage of the amount of nutrients needed according to its phenological stage.

Nitrogen is one of the main nutrients for agricultural fields, with urea being the fertilizer that provides up to 46% nitrogen in its application [29, 31]. However, the nitrogen supplied by urea is lost into the environment through the processes mentioned before, which can cause the loss from 60% to 70% of the nutrient [67]. As a result, the development of CRFs and PRFs has become an alternative to solve the problems previously mentioned and, consequently, achieve better agricultural products and a sustainable and profitable agriculture for the farmers.

Several studies, such as the work done by Ni et al. [63], have been carried out with the aim of improving the use of urea in agricultural fields and avoiding losses into the environment. Therefore, various researchers have focused on the development of coated urea for its application in crops as an alternative to avoid the N losses. Costa et al. [68] developed a CRF by coating the urea granules with polymers, which can form a barrier and delay the release of the nutrient to avoid its loss through the leaching and evaporation processes of N into the environment. The authors of this research used polyhydroxybutyrate and ethylcellulose as polymers that coated the urea granules. As a result, the researchers concluded that the coated urea granules presented a release that was 60 times slower than the uncoated urea granule had it been applied.

The urea coating from polymers that act as a barrier is an alternative to develop a more sustainable agriculture. Nowadays, the raw materials from organic sources are the ideal materials for the development of CRFs and PRFs. The entrapment, encapsulation, or coating of urea is carried out to avoid the N loss into the environment and, consequently, to improve the quality of the agricultural products. The development of sustainable agriculture aims to use materials of natural origin that have a beneficial effect on the ecosystems to improve the quality, yields, and the economy of the production.

Sulfur has been used for the controlled release of urea; however, its use is limited due to its high cost, complexity of production, and its efficacy variability, which is inconsistent in several experiments [10]. Also, the use of synthetic polymers, such as polyester, polystyrene, and polyacrylamide, presents water retention properties and favorable characteristics to be used as raw materials for the development of controlled release system of urea.

However, these synthetic polymers show disadvantages for their application in industrial quantities due to their high cost and nonbiodegradation [10]. Recent studies, such as that of Azeem et al. [10], developed a water-based polyvinyl alcohol-modified starch biopolymer to function as a controlled release urea fertilizer. They determined the urea release coefficient according to the thickness of the modified polymer shell. The authors concluded that not only the thickness of the system must be considered for the diffusion coefficient but also the heterogeneity and integrity of the polymer matrix. The studies about the fertilizers of controlled and prolonged release of urea have been carried out to determine the release coefficient values, which are possible to extrapolate and apply in agricultural fields.

Mukerabigwi et al. [69] developed a slow-release fertilizer from the coating of the urea granule with xanthan gum, guar gum, and tamarind. Additionally, the authors used epichlorohydrin as a cross-linker. After testing the three systems, the xanthan gum showed best results. This leads to the conclusion that the development of the system can be improved, and it could be effectively applied as a slow-release fertilizer. Likewise, it presents advantages, such as its biodegradability and low cost, which make it beneficial for agricultural or horticultural applications.

Biopolymers for the development of CRFs and PRFs have been studied currently for their application on agricultural fields to achieve a sustainable agriculture (Table 1). Wheat gluten is a protein network composed mainly of a monomeric protein (gliadins) and a polymeric protein (glutenin) [70]. In addition, the wheat gluten can be obtained as by-product of the starch isolation industries, and it is cheap and accessible [55]. Structurally, wheat gluten can form covalent and noncovalent bonds due to its amino acid composition, specifically the general functional groups as -NH2 and -COOH. Also, presents interaction between the R lateral chain of the glicine, proline, phenyilalanine, tyrosine, glycine, and cystein which are the main aminoacids of the wheat gluten. These interactions could be present with any other compound of interest [70, 71]. Wheat gluten is a viable alternative for the development of controlled and prolonged release fertilizers with potential application in agriculture. The natural polymeric network can be applied in combination with urea, taking advantage of the functional groups present in both compounds and achieving hydrogen bonds whereby the urea would be entrapped in the polymeric network.

On the other hand, as previously reported, wheat gluten can be considered a by-product from the starch extraction, and its use can nourish the soil of organic matter. The application of wheat gluten in agricultural fields, such as CRFs and PRFs, can be harnessed both to improve soil fertility and biochemical processes occurring in agricultural soils and, therefore, the development of plants.

5. Controlled and Prolonged Release Systems of Urea: Current Status

Controlled and prolonged release systems of urea are a potential alternative to improve the agricultural products. Recently, controlled and prolonged release systems of urea have been developed to improve the urea release into the soil and, as a result, the plant roots would absorb the necessary quantity of urea through a dosing system [72]. Table 2 shows several studies where different systems have been created to release urea to the agricultural fields.

Castro-Enriquez et al. [15] developed a wheat gluten membrane and studied its potential application as a prolonged-release system of urea in agricultural crops. The authors concluded that wheat gluten membranes could have the capacity to act as a prolonged-release system of urea in agricultural fields, reducing the environmental damages and, perhaps, increasing the yield and quality of the products.

Dall'Orsoletta et al. [13] proposed urea coated with poultry litter, and they concluded that this system does not have any effect on the nitrogen loss regardless of the soil moisture. Zhou et al. [86] developed a system of nitrogen release by adding urea into a leftover rice-g-poly (acrylic acid)/montmorillonite (LR-g-PAA/MMT) network. The results showed that this system successfully avoided the nitrogen loss from 52.3% to 19.7%. The authors found that the leftover rice could be a suitable raw material to produce biopolymers with potential applications in agriculture and horticulture.

Currently, there is a great interest in the application of nanotechnology in agriculture due to its positive effects for agricultural crops, production, and the reduction of pollution [87]. Since the procedures are affordable and present low complexity to develop controlled and prolonged release systems of urea from natural raw materials, they have drawn the attention of the scientists. On the other hand, the systems mentioned above, such as nanomaterials or biopolymer complexes, present properties that are expected from the application of biodegradable and biocompatible materials,

Table 2: Recent research on urea release systems.

Materials	Active agent	Application	References
Aminopropyltrimethoxysilane- (APTMS-) zeolite	Urea	Slow-release fertilizers	[73]
Potato starch films plasticized with urea	Urea	Delayed release system	[74]
Poly(butylene succinate) (PBS)	Urea	Slow-release nanofertilizer	[75]
Gelatin microspheres	Urea	Controlled-release fertilizer	[76]
Biobased epoxy coated urea	Urea	Controlled-release fertilizer	[77]
Microparticles from wheat	Urea	Prolonged-release system	[2]
Gluten proteins soluble in ethanol			
Wheat gluten membranes	Urea	Release system of fertilizer	[9]
Biobased elastic polyurethane	Urea	Controlled-release fertilizer	[78]
Urea-melamine-starch composites	Urea	Controlled-release of nitrogen	[79]
Urea coated hydroxyapatite by lignocellulosic bimass-extruded composites	Urea	Slow-release fertilizer	[80]
Wheat gluten microparticles	Urea	Controlled-release fertilizer	[34]
Inclusion complexes of polyester	Urea	Controlled-release fertilizer	[81]
Biodegradable oil-based polymeric coatings on urea	Urea	Controlled-release fertilizer	[82]
Cassava starch biocomposites	Urea	Controlled-release fertilizer	[83]
Wheat gluten	Urea	Prolonged-release system	[33]
Urea, chitosan, and poly (vinyl alcohol) blend	Urea	Slow-release fertilizer	[84]
Sunflower proteins, urea, and soluble polymers from industrial biowastes	Urea	Slow-release fertilizer	[85]

e.g., the improvement or maintenance of the soil fertility, ion exchange, nutrients adsorption and desorption, solubility, and precipitation of nutrients [87].

Regarding the food production in agricultural fields, it is important to keep a check on fertilizers and pesticides. As mentioned above, part of the research focuses on the improvement of agriculture based on the potential application of pesticides and fertilizers in a prolonged-release way. However, another important point is the development of nanoscale materials that function as nanosensors as these could help to monitor when the plant takes up nutrients or pesticides and calculate the time at which the application is necessary. These applications could help improve the yields, increase profits, and reduce the economic loss [88].

The materials developed to produce controlled or prolonged-release systems could have great benefits for both farmers and the environment. However, some of the benefits sought are the obtention of products at the lowest cost, high-quality products, high yields, the reduction of fertilizer, and thus, the decrease of pollution. For these reasons, the development of materials from biopolymers, such as proteins, can have a great potential to be used in agricultural fields [89]. In several researches, the production of materials from wheat gluten has focused on producing controlled or prolonged-release fertilizers with a potential application as a release system of urea. However, it still presents a great challenge in the application of materials in agricultural crops.

6. CRFs and PRFs of Urea: The Future of a Sustainable Agriculture

Conventional urea is applied into the field to nourish the plants with nitrogen. This causes the products of the agricultural sources to have the necessary quality for their commercialization [90]. However, the fertilizer loss issues are leading researchers to focus on the CRFs and PRFs (Figure 3). Since the agriculture has grown considerably worldwide and agriculture pollution is one of the main sources of greenhouse gases, the population demands better food in greater quantities which is produced through environmentally friendly procedures [91, 92].

CRFs and PRFs have been recently investigated and developed to promote the use of natural materials that could improve the nutrient distribution and decrease the loss of the nutrient into the environment [33]. The CRFs and PRFs deliver nutrients to the plants in a dosed manner according with the growth stage [91]. The reduction of nitrogen forms in the soil, such as nitrates, nitrites, and ammonium, favors the ideal consumption of nitrates and ammonium by the plants. While the nutrients are absorbed, their transformation to volatile or leachable forms decrease. Consequently, the contamination in soil, water, and air is lower than when applying conventional urea (Figure 4) [29, 31, 93]. This leads to create and try to implement sustainable agriculture, which is of great interest today due to the climate change and ecosystem care.

Nowadays, different systems have been developed to improve the fertilization process using urea in agricultural fields. Systems, such as CRFs and PRFs, can provide solutions to the problems of environmental pollution. This type of systems could help to improve the yields and the quality of agricultural products and soil. It is important to consider that the raw materials used for the development of CRFs and PRFs, such as wheat gluten, can help to nourish the agricultural soil while producing better quality food.

CRFs and PRFs are no longer a distant future; they are currently being applied and tested to achieve crop improvements. As mentioned throughout this review, many studies

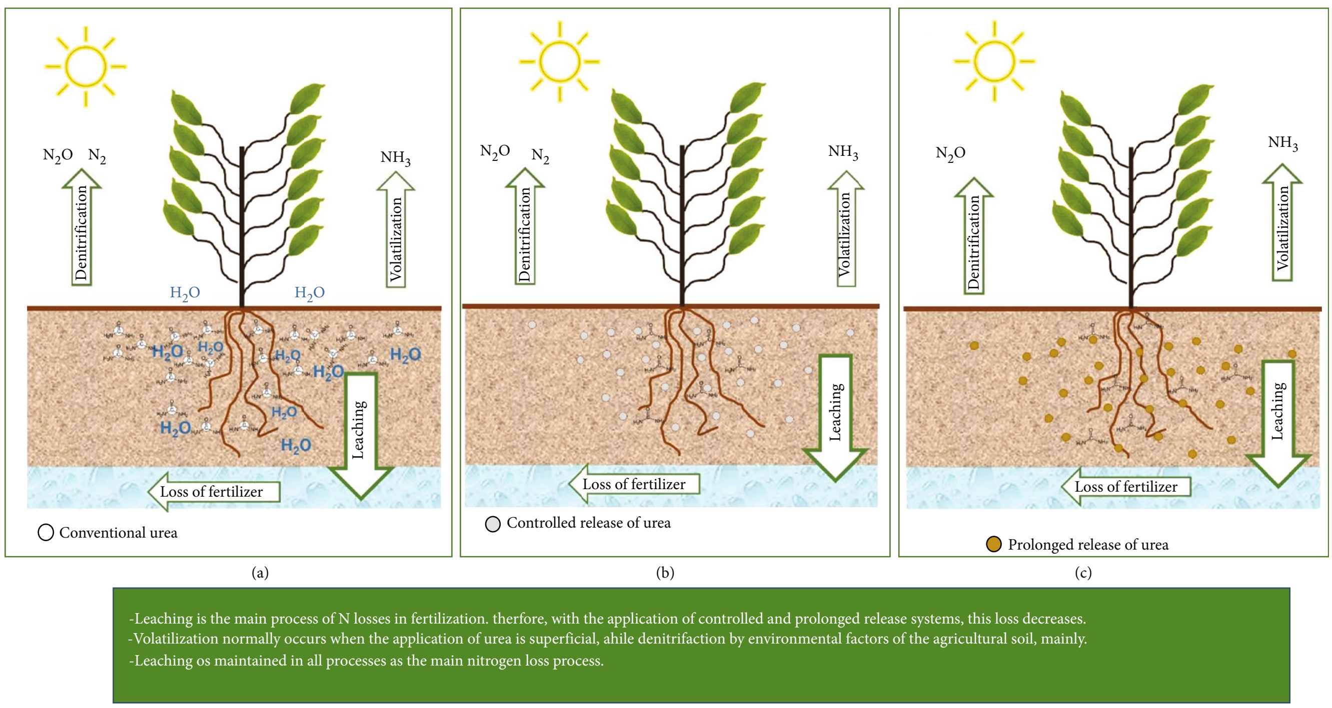

Figure 3: Three types of urea fertilization and *N* loss processes: (a) conventional urea, (b) controlled-release of urea, and (c) prolonged-release of urea.

are being carried out to know the operation, advantages, and disadvantages of their use. In addition, sustainable agriculture is slowly growing, and these systems are coming to provide an enhancement to the agricultural industry. The nanotechnology is an alternative that is growing recently to develop systems with a potential application as CRFs and PRFs.

7. Future Perspectives of the Nanotechnology in the Agricultural Fertilization

Nanotechnology has been applied in recent years to improve several areas of common life and its demands. The agricultural products are affected by the issues mentioned and explained in this review. In order to propose a sustainable agricultural in a near future, nanotechnology has been focusing on the development of nanomaterials to obtain high-quality products, decrease the environmental pollution, and improve the agricultural practices. Therefore, studies related to nanotechnology have been carried out for years. Castro-Enríquez et al. [34] developed microparticles from natural polymers, such as glutenins, with the function of prolonged-release urea fertilizers, and they demonstrated through physicochemical studies that the material has the potential to be applied in agricultural fields as prolonged-release urea fertilizer. Barreras-Urbina et al. [33] developed a system based on the mix of wheat gluten and urea. This material presents not only porosities at a nano and micrometric scale but also a water absorption capacity. Therefore, it is an attractive material to be applied as a fertilization alternative in agricultural fields.

Acharya and Pal [94] studied the applications of nanotechnology in agricultural fields, and they mentioned that the most important are nanopesticides, nanobiosensors, nanobased remediation, and nanofertilizers. In addition, the uses of nanotechnology could improve economic production, and it could be applied in different areas, such as precision agriculture, crop production, and improvement of agricultural crops. The authors indicate that the application of nanotechnology in agricultural fields needs to be further studied since reducing the costs of agricultural practices, including fertilization, is a striking factor for farmers. Nanotechnology can be an alternative to improve agricultural practices; therefore, research must continue in this area to fill in the existing gap and to prove the importance of this technology. Khan et al. [95] developed nanozeolites impregnated with macronutrients as fertilizers. The authors demonstrated the benefits of this type of fertilizer on the physical, chemical, and biological properties in soil, resulting in lettuce plants with greater foliage. In addition, after the lettuce production, there were still nutrients available for the plant.

De Silva et al. [96] produced a novel slow release of urea system based on modifying the surface of silica nanoparticles with urea. The authors saw in the developed materials an adequate slow release for more than 10 days during the experiment. The release mechanism is governed by a diffusion process. The authors concluded that the material developed could be used as a potential slow-release urea fertilizer. Alimohammadi et al. [97] evaluated the effectiveness of urea and nanonitrogen chelate (NNC) as a fertilizer on sugarcane yield and nitrate leaching in agricultural soil. The authors saw during the study that the application of NNC reduces

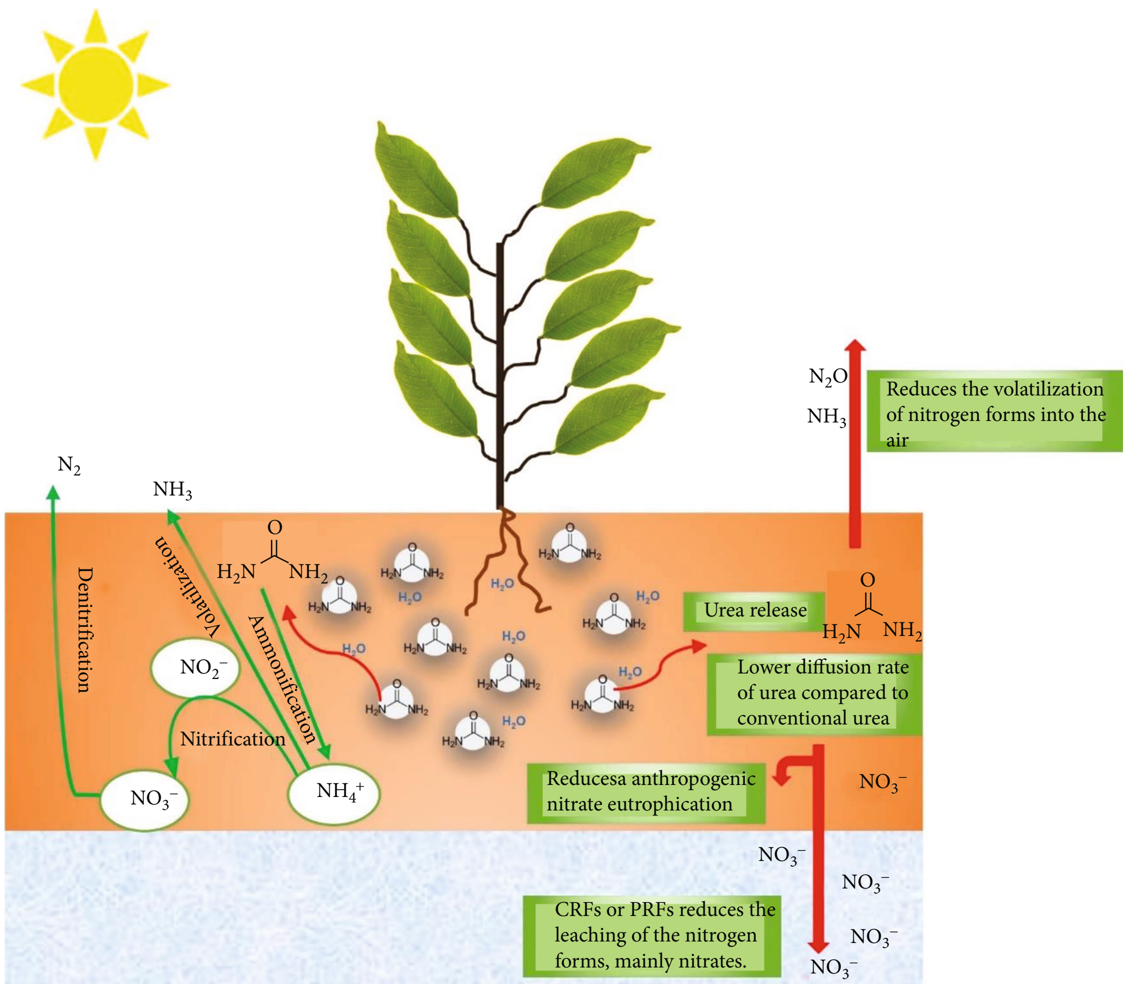

Figure 4: Reduction of the nitrogen losses into the environment using a CRFs or PRFs.

the leaching of nitrates into the environment and increases the production of sugarcane. However, they suggested that it is necessary to continue restudying these types of systems.

For many years, various studies have been carried out to improve agronomic practices. Recently, it has been the turn of nanotechnology. As mentioned throughout this review, there are many studies that are responsible for determining the effectiveness of nanomaterials with application in agricultural fields. These studies lead us to think about the great future that this science applied to agriculture, especially with the use of biodegradable and natural materials, such as wheat gluten proteins. The aim of these studies is to improve agronomic fertilization practices, reduce the contamination that this entails, achieve better quality products, and reduce costs for farmers. Nanoscience with the application of nanotechnology is the correct way to improve these practices.

8. Conclusions

Currently, CRFs and PRFs are a suitable alternative for the development of sustainable agriculture. The development of a sustainable agriculture is mainly based on the use of organic, biodegradable, and environmentally friendly raw materials, such as the polymeric network from wheat gluten. Wheat gluten is considered a by-product of the starch industry, and it presents advantages, such as low cost and availability. This biopolymer could become an ideal alternative for the development of prolonged-release fertilizers and controlled release fertilizers in agricultural fields. Nanotechnology represents an alternative method to the development of CRFs and PRFs to improve the encapsulation or entrapment process of urea, as well as the release of urea and the absorption of the nutrient by the plants. It is recommended to carry out more studies that generate quality information for the potential application of these systems to agricultural fields since, currently, it is necessary to have adequate agronomic practices to protect the environment and increase the quality and production of the agricultural products that the population demands.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there is no conflict of interest.

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