

Fabrication and Effectiveness of Composite Materials in Urea Slow-Release Fertilizers: A Mini-Review

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Abstract: The rising interest in slow-release fertilizers (SRFs) developments has been notable, particularly during the past two decades, due to the well-established environmental issue resulting from excessive fertilizer usage. Various types of self-releasing films (SRFs) have been created, encompassing physical/chemical reactions, incorporation into layered/porous materials, immobilization using hydrogels, and application of coatings and hydrogels. Numerous methodologies have been examined across various phases of development and from diverse perspectives. In the field of solid rocket fuels (SRFs), a range of approaches has been developed and implemented to assess the efficacy of their releasing capabilities. This concise overview examines the composition, modifications, and uses of biopolymer, organic, and inorganic substances SRFs designed for agricultural purposes. The review examined each material's distinctive structure and features, offering valuable insights into physicochemical and molecular arrangement. The review also offers the potential of formulations based on composite additive materials to increase crop yield, manage nutrition, and promote sustainable agricultural practices.

Keywords: composite; organic; anorganic; biopolymer; slow-release fertilizer.

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1. Introduction

The global population is projected to reach 9.6 billion by 2050, leading to a significant surge in the need for food worldwide [1]. According to estimates, there is a projected need for a 70% increase in yearly grain output to meet the global population's food needs adequately. In recent decades, the widespread utilization of agrochemicals has significantly augmented agricultural production. However, this practice has also posed challenges to human and soil well-being, leading to food availability disruptions due to diminished agricultural output. Currently, fertilizer utilization significantly enhances around 50% of agricultural output [2]. However, it is important to note that augmenting the quantity of fertilizers applied does not consistently provide a proportional improvement in crop production and yield. Agricultural activities necessitate a substantial quantity of nutrients, such as calcium (Ca), iron (Fe), magnesium (Mg), zinc (Zn), potassium (K), nitrogen (N), and phosphorus (P) to enhance soil

fertility and boost production [3,4]. However, these activities also carry the risk of causing soil contamination. Despite the escalated utilization of fertilizers, there has been a notable escalation in the rate of nutrient depletion from the soil, leading to a net-negative equilibrium of soil nutrients estimated at around 10 million tons.

Consequently, this has resulted in substantial economic detriment to farmers. The issue of nutrient shortage is a significant concern in modern times. The availability of nutrients in chemical fertilizers to plants is limited by their large particle size, resulting in reduced crop uptake.

Moreover, many macronutrients exhibit insolubility in soil, leading to the runoff of unneeded components, exacerbating water or soil pollution. Overusing chemical fertilizers provides immediate advantages in terms of increased agricultural products, though it also has long-term negative effects on nature. In the majority of instances, chemical fertilizers are applied to plants using spraying or drizzling methods, often without due consideration for the nutritional requirements of the plant or the soil. The utilization of non-targeted methods in the use of traditional fertilizers results in a substantial reduction in the number of nutrients that successfully reach the plants, while a larger quantity is lost through leaching and accidental release from agricultural fields into water bodies and soil. The use of conventional fertilizers presents additional challenges [5]. These challenges encompass financial drawbacks and ecological consequences such as compromised microflora, disturbances in terrestrial food chains resulting in genetic alterations, modifications in ecosystem dynamics, and diminished nitrogen fixation.

The utilization of composite materials has promise for a transformative impact on the agricultural industry, as it has the capacity to bring about significant changes in the food chain, enhance crop productivity, maintain ecological equilibrium, and promote environmental sustainability [6,7]. Due to their regular dimensions, solubility, mobility, and large surface area, the materials showed effective diffusion in plant cells and soil. Besides that, bacteria have demonstrated the capacity to readily translocate within plants, thereby facilitating the efficient release of nutrients [8].

Several recent review articles have examined composite materials' utilization as fertilizer coating, as shown in Table 1. Those articles discuss various aspects, including the preparation of materials, linking structure between fertilizer materials, mechanism overview, and the composite material development of SRFs in agriculture. This mini-review provides an analysis of those coating methods with the classification of the performance attributes exhibited by zeolites when employed as vehicles for delivering nutrients. It aims to enhance comprehension of nano-zeolites, encompassing their synthesis methodologies, as well as the exploitation of their physicochemical properties, including size, porosity, and thermal stability, within the agricultural sector.

Table 1. Some recent reviews about slow-release fertilizer.

Review topic	Year	Reference
Starch-based controlled/slow-release modified fertilizers (CRFs/SRFs): -Properties, structure, and grafting method of starch -Type of starch (cassava, maize, tapioca, corn, potato) -Biodegradation	2023	[9]
Cellulose nanofibril (CNF) as hydrogel incorporating slow-release fertilizer: - Cellulosa properties and limitations - Nanocellulose and CNF	2023	[10]
Biochar-based slow-release fertilizer: - History evolution and synthesis method of biochar - Mechanism of loading in nutrients	2022	[11]

Review topic	Year	Reference
Lignin-based slow-release fertilizer: <ul style="list-style-type: none">- Lignin properties and characterization- Mechanism cross-linking fertilizer-lignin	2022	[12]
Zeolite as smart nutrient delivery-based slow-release fertilizer: <ul style="list-style-type: none">- Nanofertilizer for modern agricultural practices- Zeolite type and synthesis	2022	[13]
Cellulose-based controlled-release fertilizer <ul style="list-style-type: none">- Release rate by permeation, absorption, and chemical- Plant growth regulator	2019	[14]
Composite materials additive in slow-release fertilizer <ul style="list-style-type: none">- Organic- Inorganic (zeolite, silica, char, clays)- Biopolymer (starch, lignin, cellulose)	This review	

2. Slow-release fertilizer

Conventional nitrogen fertilizers typically release excessive amounts of ammonium or nitrate ions that are readily available to plants shortly after they are applied to the soil. However, plants do not effectively utilize a substantial fraction of these ions. The surplus of ammonium can be easily vaporized, but nitrate is prone to leaching due to its high solubility and weak attraction to soil particles. Utilizing slow-release fertilizers (SRFs) has proven to be a viable strategy for mitigating nitrogen losses by extending the duration of nutrient release with the specific requirements of plants [15].

Controlled-release fertilizers (CRF) and slow-release fertilizers (SRF) have been formulated to delay and regulate nutrient release, thereby prolonging their accessibility for crop growth cycles. Using these fertilizers minimizes nutrient losses and root damage compared to conventional methods, resulting in enhanced fertilizer efficiency. CRF can be employed when the elements that govern and control the speed, arrangement, and length of nutrient discharge are clearly defined and controllable throughout the production of CRF. In addition, SRF exhibits a slower nutrient release rate than traditional fertilizers. However, the level of precision in controlling the pattern, duration, and release rate is not as high [16]. According to the internationally recognized standard ISO18644, fertilizer is categorized as CRF based on three distinct criteria outlined in the standard. Initially, within the initial 24-hour period subsequent to its application, the fertilizer mustn't exceed the release of more than 15% of its nutrient content. The parameters mentioned above serve to guarantee that the fertilizer facilitates the slow and controlled release of nutrients over a specified timeframe. This controlled release mechanism is designed to enhance plant development to its maximum potential while limiting any potential losses or leaching of nutrients.

Nowadays, polymer-coated fertilizers are extensively employed slow-release fertilizers (SRFs) due to their ability to predefine the release rate during the formulation process such as including polyester, epoxy, polyurethane (diisocyanate), and sulfur [17,18]. A protective coating is applied around the granule to act as an obstacle, effectively inhibiting direct physical interaction between the active ingredient (N fertilizer) and water. The process of water diffusion into the coated membrane facilitates the dissolution of nutrients, therefore enabling their gradual release from the membrane. Cured polyester resins have favorable attributes, including enhanced mechanical, chemical, and heat-resistant capabilities. An unsaturated polyester (UP) is a thermosetting polymer with remarkable attributes, including outstanding abrasion resistance, hydrophobicity, and mechanical properties. Different types of petroleum and bio-based polyester resins have been used to create solid-recovered fuel (SRF). A

waterborne polyester synthesis was carried out using a poly-condensation procedure that involved citric acid, glycerol, and dimer acid. The polyester coating demonstrated significant attributes, including high tensile strength, impact resistance, fracture strain resistance, thermal stability, and efficient control of urea release. Additionally, this process enhances the composite polymers' biodegradability while maintaining the polymer's advantageous features as a coating material [19].

There exist four distinct types of CRF based on their structural characteristics. There are several methods for controlling the release of water-soluble fertilizers. One approach involves the use of physical barriers, such as the formation of a matrix or coating. Another method involves using low-solubility inorganic materials such as $(\text{NH}_4)_3\text{PO}_4$. In addition, low-solubility materials that can be biologically or chemically degraded, such as urea form, can be used.

Moreover, materials that have a moderate level of solubility and breakdown at a slow rate in soil can also be employed. The second type of CRF technology involves utilizing modified inorganic materials, which often possess superabsorbent qualities. This emerging material technology is now under development [19].

Endophytic bacteria inhabit different plant tissues and perform diverse roles, such as nitrogen fixation, phosphorus solubilization, augmentation of host defense mechanisms, synthesis of plant growth-regulating compounds, and bioremediation [20]. Endophytic bacteria have been scientifically proven to significantly impact maintaining the microecological equilibrium inside the host, boosting its resistance and facilitating the healthy development of the host plant. Furthermore, endophytic bacteria enhance the process of Hg phytoremediation by regulating the accumulation and release of Hg. Metagenomic studies have demonstrated that the plant endo microbiome is influenced by various parameters, including soil type, organ type, phenological stage, plant species, and fertilization [21].

3. Biopolymer based slow-release fertilizer

The application of thin polymeric films to coat fertilizers represents a straightforward yet efficient method for achieving controlled release of nutrients. The rate at which nutrients are released through a thin polymeric coating film is contingent upon various factors, including the composition of the coating components, the texture of the film, and its thickness. Besides petroleum-based synthetic materials, commonly used biopolymer coating in slow-release fertilizers such as chitosan [22,23], gum [24], artemia egg [25], lignin [26], and cellulose [27]. Hence, a sustainable solution would involve using biomaterials to produce solid recovered fuels (SRFs); commercial applications are predominantly derived from petroleum-based synthetic materials. Various bio-based coating materials, including cellulose, starch, chitosan, and fatty acids, have been employed in sustainable release formulations (SRFs). The utilization of wheat straw-derived slow-release fertilizers (SRFs) was observed to significantly impede the rate of nutrient release, with around 67.6% of nutrients being released over a period of 30 days. A starch-based superabsorbent was employed to prepare the SRFs. However, the release of the superabsorbent was quite quick, with 70% of the release occurring over a span of 4 days. Biomaterials typically exhibit hydrophilic properties, rendering them susceptible to disintegration when exposed to high levels of water content in soil.

Consequently, this might lead to uncontrolled release of nutrients and subsequent loss thereof. Therefore, to preserve the coatings' integrity and prevent excessive dissolution, it is more suitable to utilize bio-materials having hydrophobic properties as coatings for SRFs.

Natural rubber (NR) is a hydrophobic biopolymer, commonly referred to as the Pará rubber tree, consisting of polyisoprene. It is commonly found in the form of latex, making it a convenient material for producing thin film coatings [27].

3.1. Lignin-based SRF.

Lignin is the next most abundant biomaterial after cellulose, in terms of abundance. Lignin exhibits an amorphous nature and is somewhat hydrophobic, characterized by a 3D structure encompassing carboxyl, phenolic hydroxyl, aliphatic hydroxyl, and methoxy functional groups. Lignin as a coating material has been employed for SRFs due to its cost-effectiveness and widespread availability [12]. Nevertheless, the presence of a particulate lignin structure and the absence of functional groups necessary for bonding result in the occurrence of film flaws in the coating of SRFs. The release of urea from lignin-SRFs was deemed suboptimal, as the total release of the fertilizer occurred within a 25-minute timeframe. Hence, certain changes are necessary to optimize the utilization of lignin as a covering for solid recovered fuels (SRFs). These modifications may include surface functionalization or the creation of composites by combining lignin with other chemicals. In order to mitigate the release of nitrogen from lignin-based solid recovered fuels (SRFs), acetic acid was added to acetylated sulfite lignin, obstructing the hydrophilic groups. A comparatively lower rate of nitrogen release was observed, resulting in a release of 45.3% within a period of seven days. A coating substance, disulfide on lignocellulosic (BCSPU), was developed to extend the duration of nitrogen release. The release percentage of Nitrogen from BCSPU was found to be 61.5% over a period of 63 days [28].

Lu *et al.* [28] stated that physically hindered lignin-based slow-release fertilizer involves the utilization of a physical barrier and the adsorption of coated material to achieve a slow-release effect. Applying a physical coating serves the purpose of impeding the ingress of water into the central core of the fertilizer while concurrently hindering the outer dispersion of nutrients. The release of nutrients from physically hindered fertilizer occurs through either a rupture mechanism (Figure 1a) or a diffusion process (Figure 1b). In the process of rupture release, water infiltrates the coating, leading to the dissolution of nutrients.

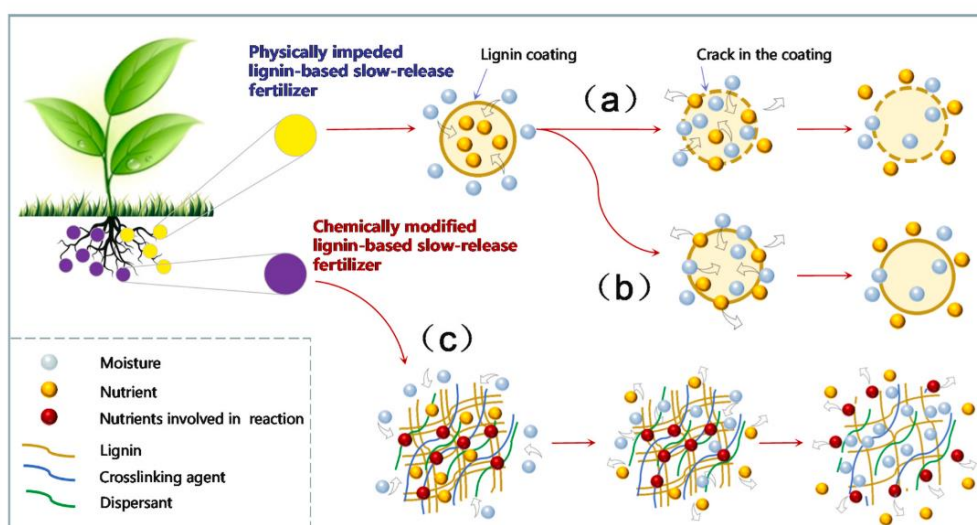


Figure 1. Slow-release fertilizer mechanism in nutrient release: (a) rupture; (b) diffusion; (c) chemical modification. Reproduced from ref. [12] with permission from Elsevier B.V. Copyright 2022.

This subsequently creates a significant osmotic pressure gradient between the internal and external layers of the coating, ultimately resulting in the rupture of the coating and the

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subsequent release of nutrients (as depicted in Figure 1a). The driving mechanism behind the diffusion release is attributed to the disparity in nutrient concentration between the interior and exterior of the coating (Figure 1b).

Boonying *et al.* [26] synthesized a slow-release fertilizer (SRF) coating made from a composite of lignin and natural rubber (Li/NR) that has been modified with natural rubber-graft-polyacrylamide (NR-g-PAM) was produced. Several coating films were produced using NR-based materials, including NR-g-PAM, Li/NR, and Li/NR modified with NR-g-PAM (Li/NR-g). The results showed that there was an increase in water absorption as the NR-g-PAM content in Li/NR increased. The release of nitrogen from urea pre-coated with ethyl cellulose, compared to a complete release in water within 1 hour, was significantly extended to over 700 hours when coated with Li/NR-g on slow-release fertilizers (SRFs). When the NR-g-PAM content is below 25 phr, the transport of N through Li/NR-g coatings is mostly controlled by relaxation, resulting in a relatively sluggish release of N. When the NR-g-PAM concentration in Li/NR-g coatings was above 25 phr, the diffusion process became more prominent than relaxing, leading to a rise in the release of N. The Li/NR-g10 coated urea exhibited a significantly delayed release of nitrogen (N) in the soil, with just 60% of the total N being released after 112 days. The morphology of the samples is depicted in Figure 2.

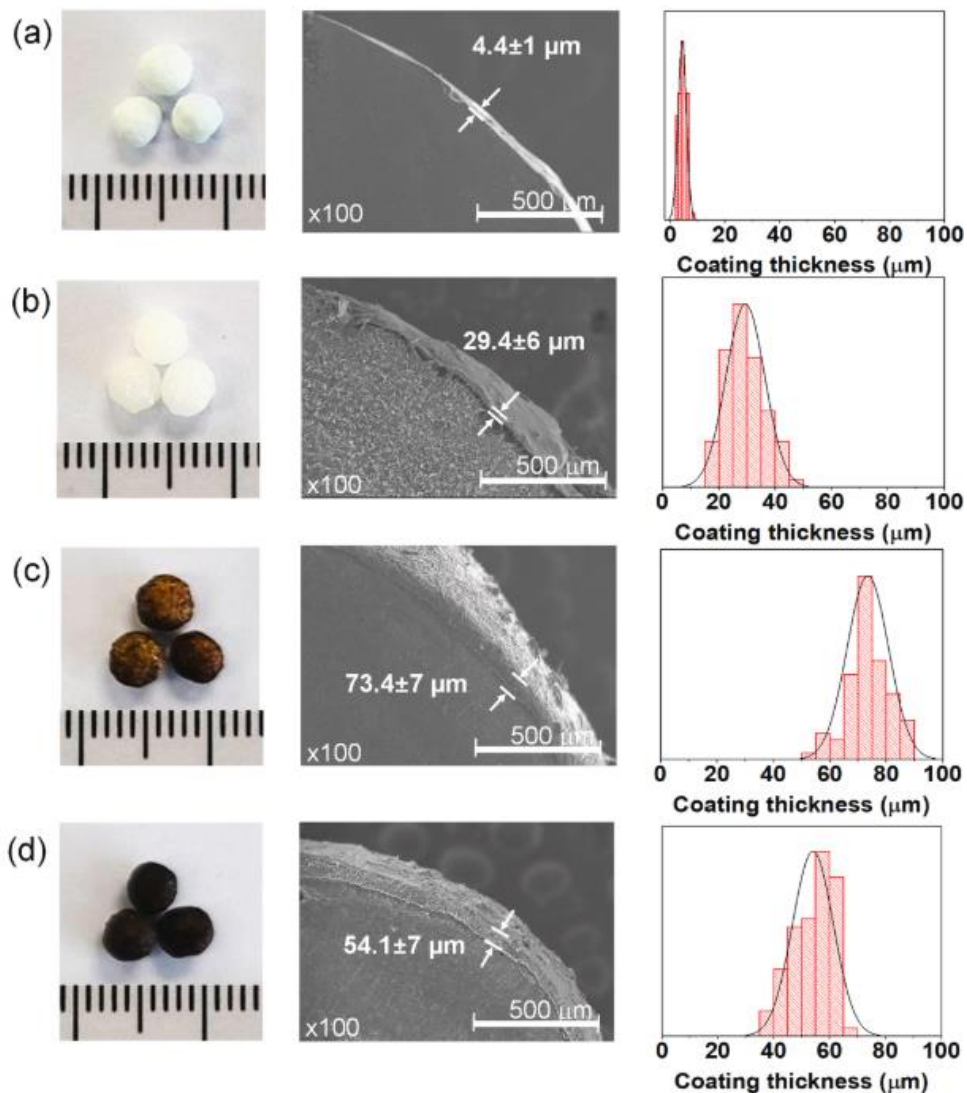


Figure 2. The polymeric-fertilizer photos, cross-sectional SEM images, and coating thickness of (a) ethyl cellulose coated urea; (b) NR-g-PAM coated urea; (c) Li/NR coated urea; (d) Li/NR-g10 coated urea.

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3.2. Starch-based SRF.

Starch is a biopolymer composed of renewable natural polysaccharides. Its notable attributes include biodegradability, widespread availability, and environmentally beneficial characteristics [29]. The hydrophilic character, network structure, and capacity to establish strong hydrogen bonds with water molecules of the starch-based hydrogel may substantially enhance the soil's water-holding capacity. Consequently, the application of hydrogel fertilizers to soils would result in increased water retention. Plants predominantly comprise starch, which is a polymer composed of two distinct forms of glucans, namely amylose and amylopectin. The polymers under consideration are present in the form of granules with varying sizes, which can be classified into three categories based on their dimensions: A-type (big), B-type (medium), and C-type (small). These granules exhibit a wide range of shapes and dimensions. The organization of starch granules is characterized by the presence of concentric layers comprising both semi-crystalline and amorphous regions [9]. The presence of variations in the chemical composition, such as α -glucans, moisture, lipids, proteins, and phosphorylated residues, as well as structural differences, in starches derived from different sources and even within the same type of starch, have a direct correlation with the surface properties, hardness, and crystallinity of the granules. The presence of amylose has an effect on the arrangement of amylopectin molecules into crystalline structures and the arrangement of these structures within starch granules [30].

Furthermore, starches that possess a higher amylose content exhibit greater exothermicity and have the potential to produce a more enduring amylose-lipid complex [31]. This complex, in turn, influences thermal characteristics and the gel formation process. Figure 3 represents the process of manufacturing starch-g-PAM SAPs and then loading urea. The soil's management of nutrient release rate is influenced by two primary factors: the network structure and strength of hydrogels. Hydrogels with non-uniform cross-linked network structures exhibit diminished mechanical properties, affecting solvents' infiltration and the kinetics of mass transfer within the network structure. Therefore, researchers have consistently pursued the development of hydrogels with spatially homogeneous architectures. The polymer chain's cluster size, distribution, and architecture have been identified as factors that govern the connection homogeneities.

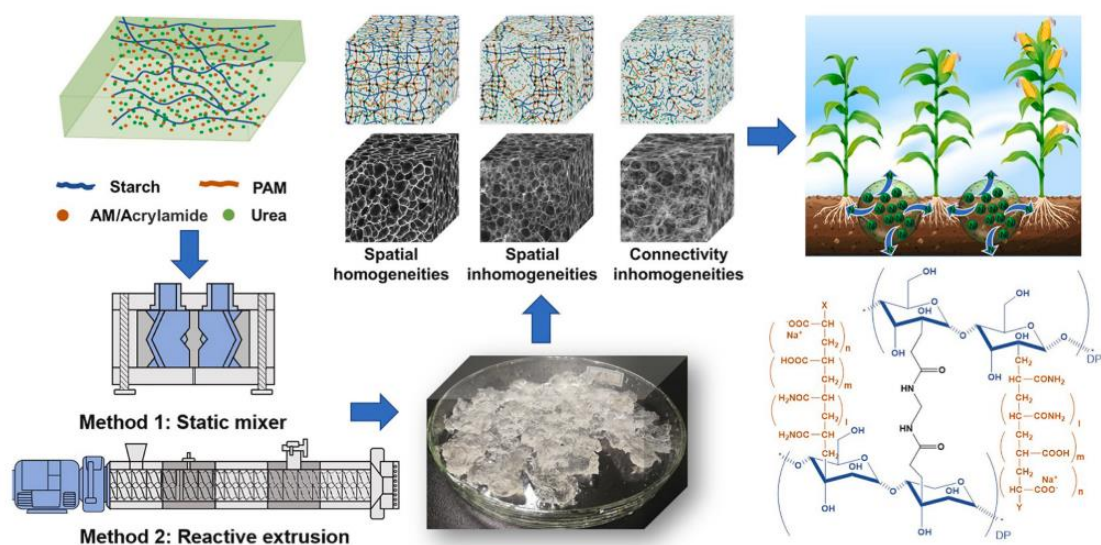


Figure 3. Schematic illustration of urea-starch-g-PAM synthesis. Reproduced from ref. [5] with permission from Elsevier B.V. Copyright 2023.

Zafar *et al.* [32] employed a combination of starch and polyvinyl alcohol (PVA) with acrylic acid (AA), citric acid (CA), and maleic acid (MA) to coat urea prills. Various coating formulations were synthesized and subsequently utilized for treating urea prills. These formulations included urea coated with starch (10%) and polyvinyl alcohol (5%) in combination with acrylic acid at concentrations of 2%, 4%, and 6% (referred to as USP-A2, USP-A4, and USP-A6, respectively).

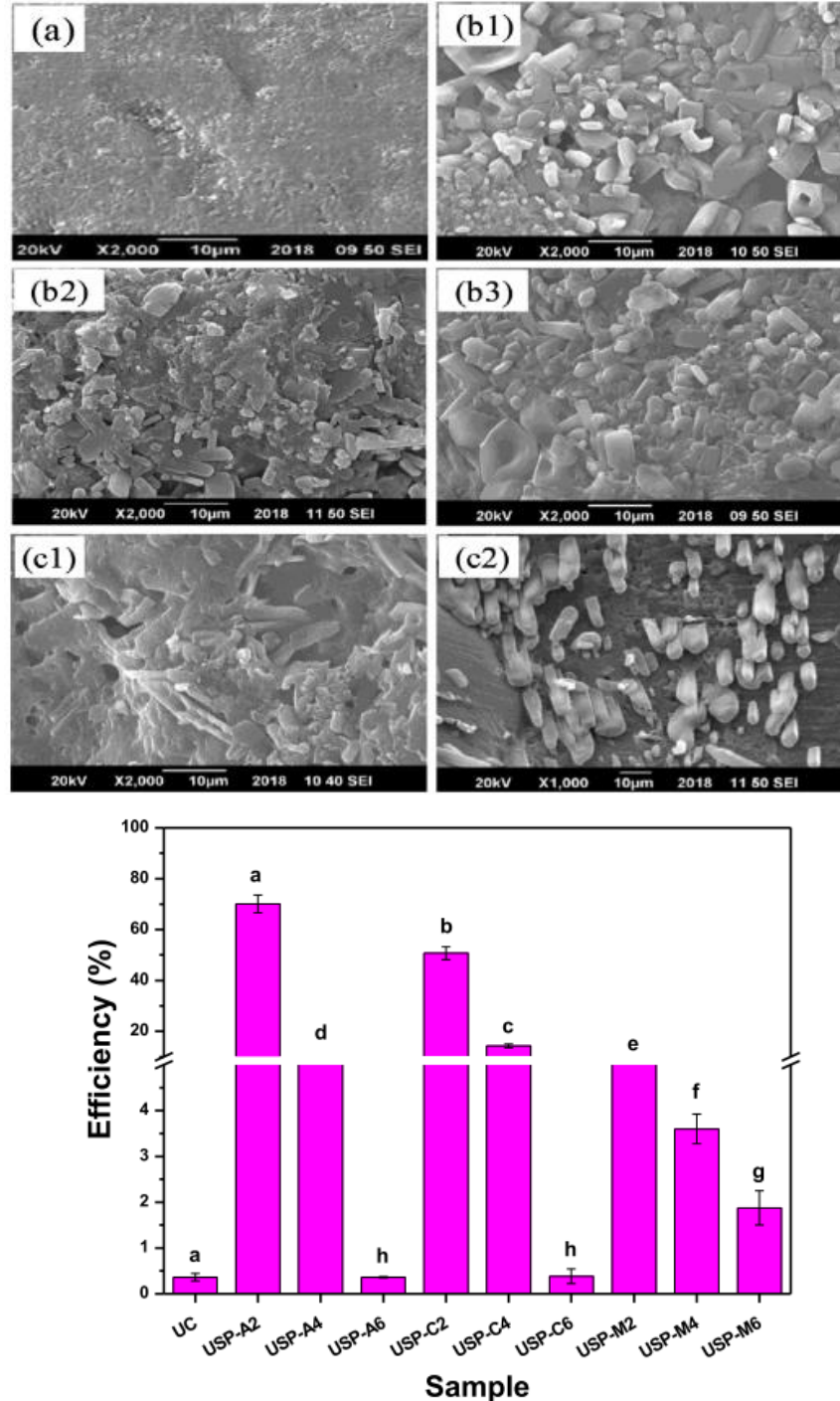


Figure 4. The SEM analysis of (a) urea without coating; (b1) USP-A2; (b2) USP-A4; (b3) USP-A6; (c1) USP-C2; (c2) USP-C4, and the release efficiency. Reproduced from ref. [32] with permission from Elsevier B.V. Copyright 2021.

Additionally, citric acid was employed at concentrations of 2%, 4%, and 6% (designated as USP-C2, USP-C4, and USP-C6), and maleic acid at concentrations of 2%, 4%, and 6% (referred to as USP-M2, USP-M4, and USP-M6). Following the urea coating process

in a fluidized bed coater, the subsequent analysis involved characterizing both uncoated and coated urea samples. Out of all the urea-coated samples, USP-A2 and USP-C2 exhibited the greatest crushing strengths, measuring 12.08 and 13.67 N, respectively, as exhibited in Figure 4. Additionally, USP-A2 demonstrated a nitrogen release efficiency of 70.10%, while USP-C2 exhibited a nitrogen release efficiency of 50.74%. Applying coating to urea samples resulted in enhanced foliage production, chlorophyll content, N-uptake, and apparent nitrogen recovery (ANR) in spinach plants compared to those treated with uncoated urea and the control group. Nevertheless, the coated samples, specifically USP-A2 and USP-C2, exhibited favorable outcomes in terms of dry foliage output (2208 ± 92 and 2428 ± 83 kg/ha), chlorophyll content (34 ± 0.6 and 34 ± 0.4 mg/g), nitrogen uptake (88 ± 4 and 95 ± 6 kg/ha), and apparent nitrogen recovery (59 ± 4 and $67 \pm 6\%$). Hence, the utilization of urea prills coated with a blend of biodegradable polymers presents a more favorable option for farmers seeking to optimize agronomic yields by regulating fertilizer nutrient release rates.

3.3. Cellulose-based SRF.

Cellulose, a natural polymer, can be transformed into a superabsorbent polymer by undergoing grafting modification on its main backbone [33]. The grafting polymerization process encompasses various approaches, including photo-grafting, irradiation, and chemical start. Cellulose can be extracted from waste or plant [34]. The rice straw comprises silica (70.8%), hemicellulose (33.8%), cellulose (36.5%), lignin (12.3%), ash (13.3%), and extractive compounds (3.8%). Cellulose nanofibril-coated fertilizers have both direct and indirect effects on plant development. Indirect methods (as seen in Figure 5) encompass three distinct actions: 1) Adjusting the pH of the soil to approximately 7, facilitating plant access to nutrients; 2) Enhancing the abundance of microbial biomass, particularly nitrogen and carbon, to promote nutrient cycling and mitigate the adverse effects of agrochemicals and pollutants; 3) Enhancing nutrient availability in the soil by minimizing nutrient-soil interactions.

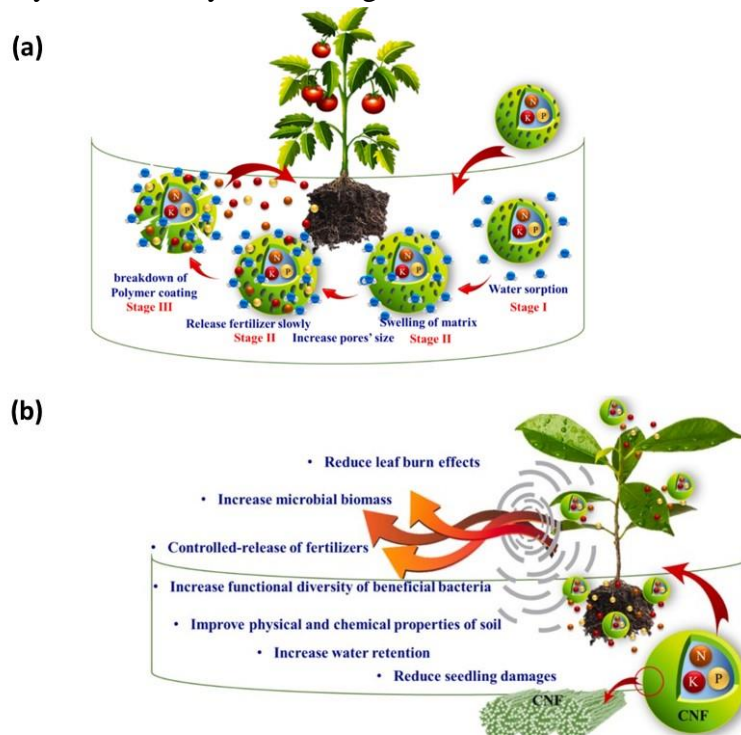


Figure 5. (A) slow-release fertilizers mechanisms; (B) fertilizer of CNF/cellulose nanofibrill impact on the plant. Reproduced from ref. [10] with permission from Elsevier B.V. Copyright 2023.

Moreover, the presence of essential nutrients can be controlled by applying fertilizers.
 4) Improving the soil's capacity to retain water and moisture using cellulose nanofibrils as a highly efficient superabsorbent hydrogel [34].

4. Organic-Based Slow-Release Fertilizer

Currently, slow-release fertilizers are primarily categorized into two types: inorganic-coated fertilizers and organic-coated fertilizers [35,36]. The current polymer coating materials utilized in various industries have traditionally been derived from petrochemical sources, including polyurethane, epoxy resin, and polyethylene [37]. Shi *et al.* [38] aimed to create a solvent-free UV-curing roller coating process for producing bio-based superhydrophobic polymer coatings used in slow-release fertilizers. The acrylate epoxidized soybean oil monomer was subjected to UV irradiation in the presence of $Mg(OH)_2$ modified with stearic acid and subsequently added with hydrophobic filler, i.e., paraffin wax depicted in Figure 6. The hydrophobic characteristics of the poly-epoxidized soybean oil acrylate (PESOA) coating were improved by modifying it with stearic acid@ $Mg(OH)_2$ and paraffin wax after being exposed to UV irradiation for 30-60 seconds. This was demonstrated by a contact angle measurement of $150.4^\circ \pm 1.25^\circ$. At a concentration of approximately 7%, the coating substance exhibited an initial release rate of only 1.625%. However, the duration of nitrogen release was considerably prolonged, reaching a high of 63 days. The utilization of UV-curing technique presents a novel and uncomplicated approach for the synthesis of economically viable slow-release fertilizers derived from bio-based sources.

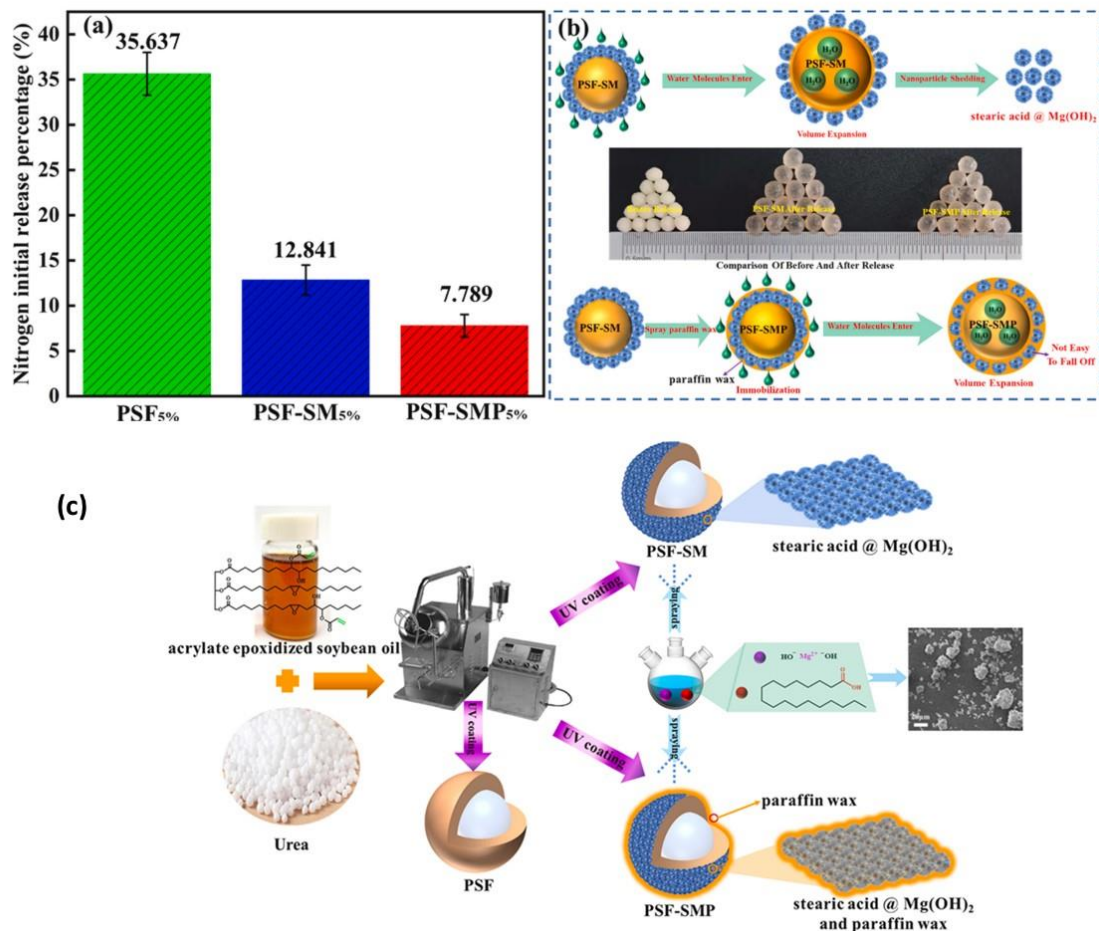


Figure 6. (a) efficiency of PSF fertilizer; (b) Illustration of mechanism properties; (c) Synthesis process. Reproduced from ref. [38] with permission from Elsevier B.V. Copyright 2022.

5. Inorganic based slow-release fertilizer

Moreover, the application of fertilizers plays a vital role in the growth and development of crops. According to Chen *et al.* [39], inorganic fertilizer, which is rich in nutrients, can potentially increase agricultural productivity and boost overall crop quality. Maghsoodi *et al.* [40] explained that the gradual release of nitrogen from a combination of urea and inorganic material (hydrocar, zeolite, biocar, and hydroxyapatite) can be comprehended through diverse elucidations: 1) Urea leaching from the root zone is hindered by the infiltration of urea into pores. 2) The presence of urea in the soil leads to a decrease in its interaction with soil enzymes, causing a delay in the conversion of urea into NH_4^+ ions. 3) NH_4^+ ions are absorbed into the pores' exchange sites, hence impeding their transformation into nitrite and nitrate by nitrifying bacteria. In addition, the rate of urea release can be regulated by the size of the pore rock chips, with bigger sizes resulting in slower release. Alikhani *et al.* [41] also stated that carbon dots (CD) could be used to alter the Zn release and increase root-shoot biomass, fertile spikelet, and grain yield by 20, 44, 16, and 43%, respectively, compared to ZnSO_4 treatment.

5.1. Zeolite.

Zeolites, which are porous aluminosilicates, exhibit high potential as viable candidates for employment in nutrient transportation [42]. Zeolites can be found in nature or produced through chemical synthesis [43]. The porosity level in zeolites can be adjusted at the nanoscale to meet specific application needs. Naturally occurring zeolites encompass a variety of species, such as sodalite (SOD), beta-structured (BEA), mordenite (MOR), clinoptilolite, and lind type A (LTA) [44–46] with variations in terms of their pore diameters, ion exchange characteristics, and bulk densities [47]. In contrast, synthetic zeolites are fabricated using several procedures such as hydrothermal, template-free, and template-assisted. Zeolites, as smart carriers in nanofertilizers (Figure 7), possess distinctive characteristics that facilitate the extended and regulated delivery of essential nutrients to the soil, including K, NH_4^+ , and PO_4^{3-} [48,49].

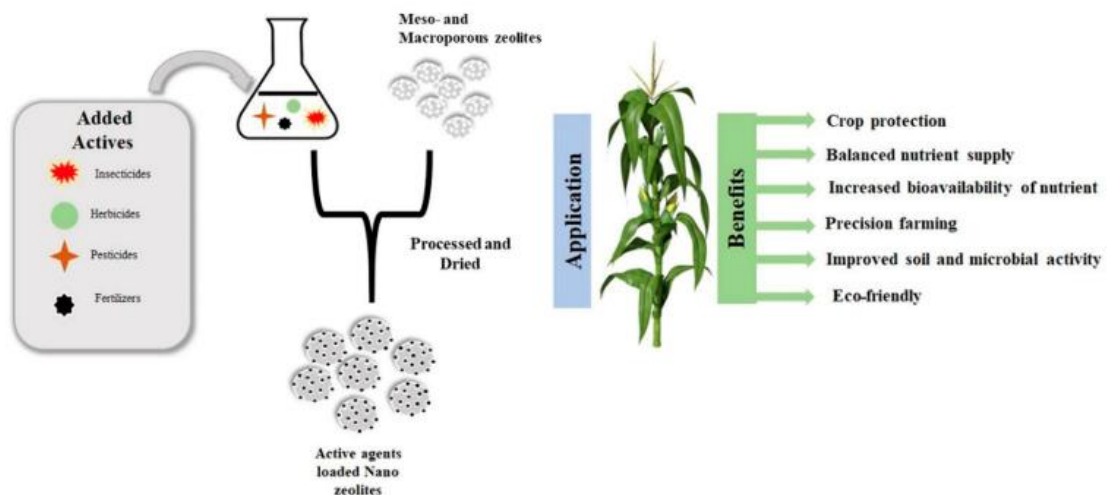


Figure 7. Zeolite as a carrier and slow-release fertilizer. Reproduced from ref. [13] with permission from the Multidisciplinary Digital Publishing Institute (MDPI). Copyright 2022.

Sun *et al.* [50] employed a natural zeolite consisting of 15% geolyte and 85% clinoptilolite to mitigate the environmental hazard of heavy metals from organic fertilizer. Including 2.5% zeolite decreased the mobile Cu, Pb, and Cd portions, including the soluble, exchangeable, and carbonate-bound fractions. Adding zeolite to organic fertilizer ensured the

stabilization of heavy metals, resulting in an environmentally friendly way of utilizing organic matter in the soil.

Maghsoodi *et al.* [40] explained urea exhibited materials (UH, UB, UZ, U-HAP)-carriers interaction, hence regulating the release of urea and significantly decreasing the release of urea by factors of 4.5, 6.5, 9.0, and 11.5, respectively, compared to the urea-only treatment. After applying UH, UB, UZ, and U-HAP to the soil (Figure 8), the cumulative release was found that 89.9%, 76.5%, 75.0%, and 58.1% of the urea had been converted to NH_4^+ after 20 days indicated that the UB, UZ, and U-HAP exhibited a gradual release of urea, potentially leading to a decrease in nitrogen loss and an improvement in its use efficiency in calcareous paddy soils.

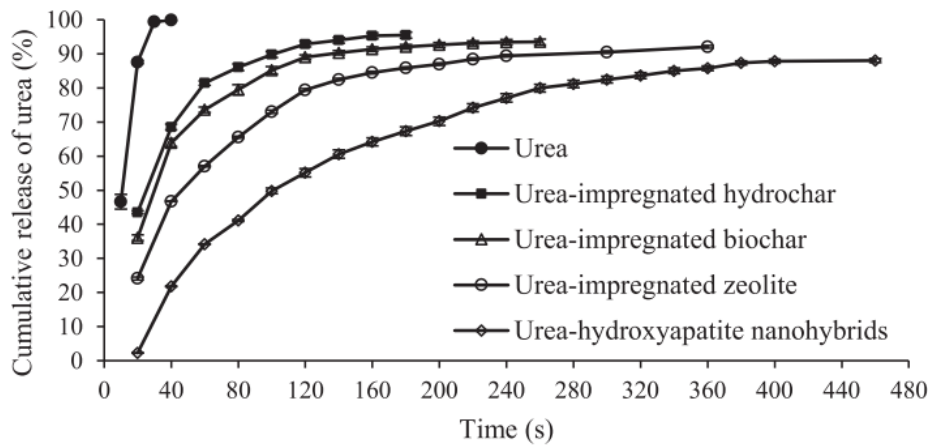


Figure 8. The release behavior of urea with inorganic materials. Reproduced from ref. [40] with permission from Elsevier B.V. Copyright 2020.

Khan *et al.* [51] also demonstrated that the positive impacts of the NZCF treatment on lettuce plants (Figure 9) can be attributed to the enhanced chemical, physical, and biological characteristics of the soil. Moreover, the treatment ensures a continuous supply of nutrients, as indicated by decreased soil pH, higher total dissolved solids (TDS), improved water retention, and increased availability of elements for absorption by plant roots.

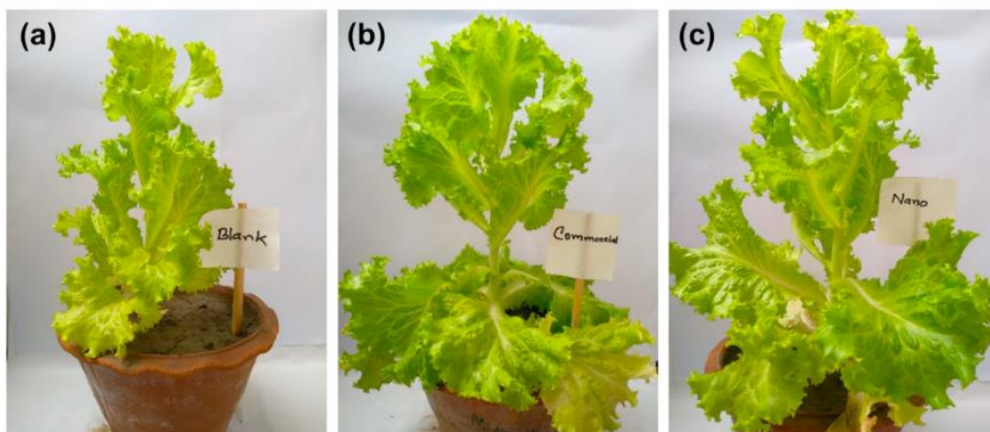


Figure 9. Lettuce plants images: (a) without fertilizer; (b) NPK as commercial fertilizer treatment; (c) NZCF treatment. Reproduced from ref. [51] with permission from Elsevier B.V. Copyright 2021.

5.2. Biochar.

Biochar is a solid substance derived from the thermochemical conversion of biomass inside an environment with limited oxygen availability [52]. Biochar exhibits many

characteristics, including carbon content ranging from 23.6% to 87.5%, pH levels ranging from 5.2 to 10.3, cation exchange capacity of 10-69 mol/ kg⁻¹, and surface area of 0-642 m² g⁻¹ [53]. Adding biochar to soil has numerous advantages, including the enhancement of the control of plant diseases, biological-physicochemical properties, the improvement of soil fertility and crop output, and the containment of organic/toxic metal pollutants. In addition, the application of biochar has the potential to enhance the availability of nutrients in the soil, raise the cation exchange capacity and water retention capacity of the soil, and improve the composition and activity of soil microbial communities [54]. BSRNFs or biochar-based slow-release nitrogen fertilizers release nutrients could be prepared by a ratio of 2:1 (carbon and Na-Alg and carbon) to achieve a span of 74 days and a cumulative nitrogen release of 65.91% [55]. Banik *et al.* [52] stated that more than 99% of the urea was released from the urea-uncoated within the same time period depicted in Figure 10. The release of urea from UAN fertilizers and S-coated urea during a 1-hour time interval was 82% and 73%, respectively. The probable cause for this observation is the decreased contact between urea and water within the SRF pellets. Following other studies that explained biochar-coated urea, the results also exhibited enhanced resistance to wear, moisture, and compression as the biochar-fertilizer ratio increased [56].

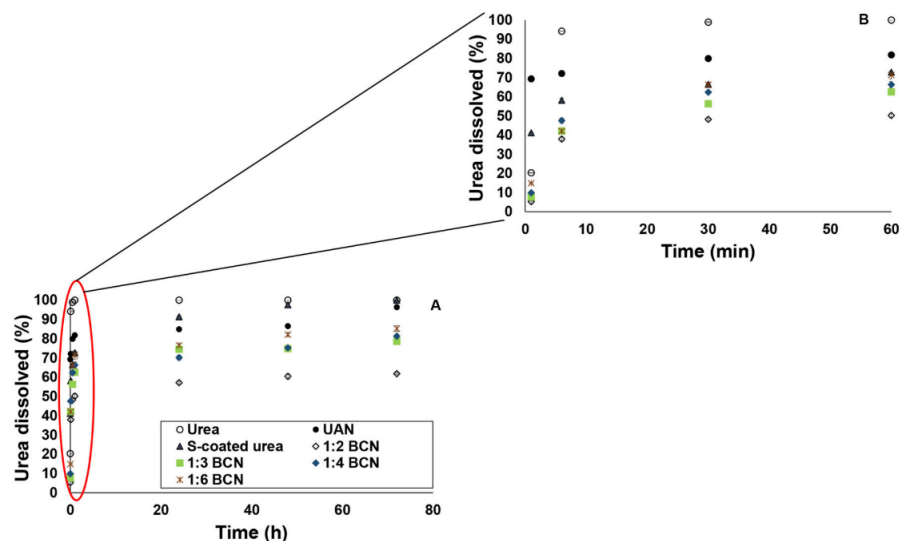


Figure 10. Comparison of urea dissolved between uncoated and biochar coated. Reproduced from ref. [52] with permission from John Wiley & Sons Inc. Copyright 2023.

5.3. Silica.

Porous materials such as silica have consistently demonstrated efficacy in a range of applications, particularly in the field of biology, where mesoporous silica in drug delivery has garnered significant attention [57]. The utilization of this substance as a reservoir for fertilizers has been constrained mostly to discrete particles that are regulated via diffusion. Bindra *et al.* [58] have prepared composite material consisting of urea-loaded fiber@SiO₂ and exhibits a chlorophyll content increase of around 3 times and 1.25 times on day 10th for rice yield, in comparison to urea and urea-fiber treatments, respectively. The study observed the nitrogen concentrations in plant leaves during 10 days following the administration of urea in three different forms: (1) urea incorporated in the fiber, (2) urea incorporated in the composite, and (3) free urea application (Figure 11) in a sample of 23 various forms. This observation aligns with the fast liberation of nitrogen from the unprotected urea fertilizer.

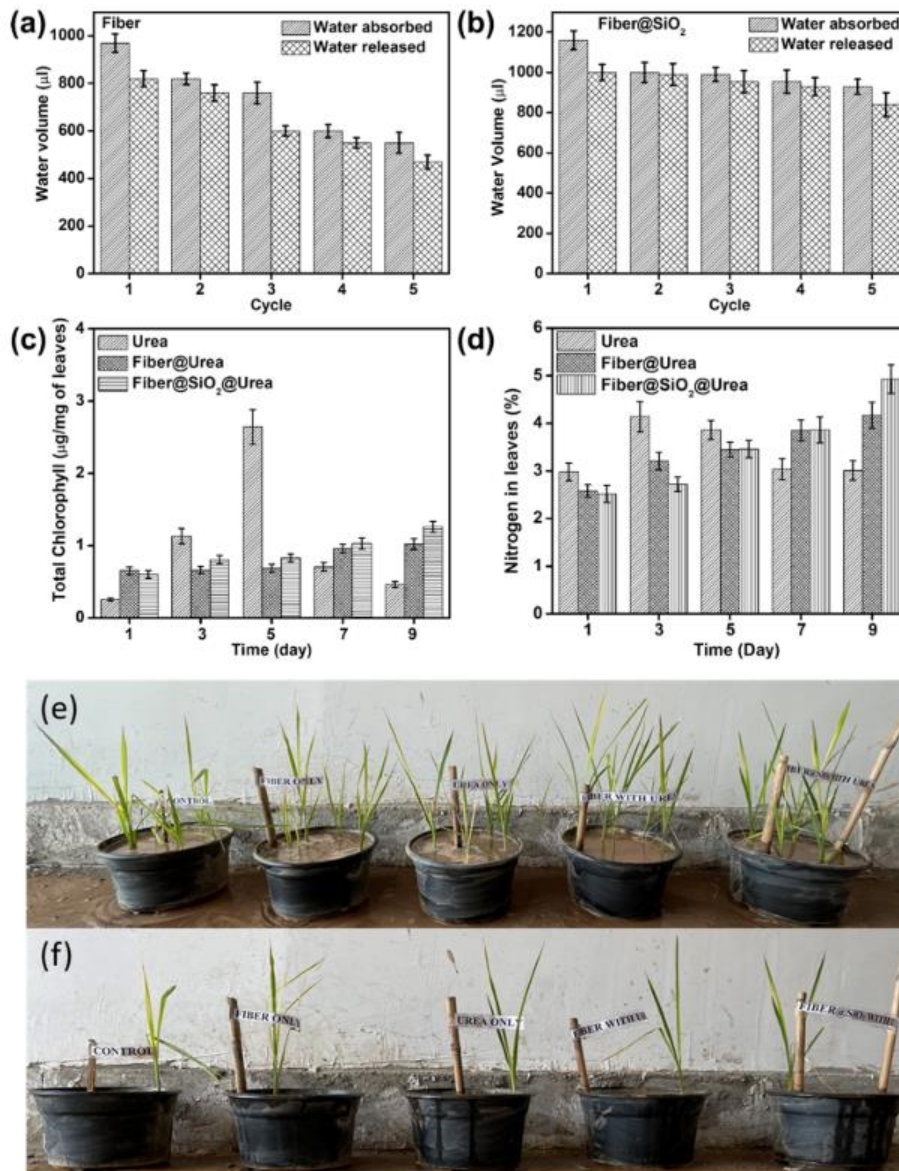


Figure 11. The efficiency study of fiber-SiO₂ fertilizer (a-b) water absorption capacity; (c) chlorophyll content; (d) nitrogen content; (e,f) rice plants photos in day 1-5. Reproduced from ref. [58] with permission from American Chemical Society. Copyright 2022.

5.4. Clays.

The utilization of clay minerals such as smectite, saponite, glauconite, dolomite, montmorillonite, and bentonite as inorganic substances is of interest for this particular objective, owing to their chemical structure which imparts them with both expandable and changeable qualities [59–61]. Faishol *et al.* [62] synthesized a composite material by combining polymer-modified clay and alginate-saponite. The objective was to create a slow-release fertilizer for urea by incorporating alginate into the structure of saponite (as shown in Figure 12) using a 1:1 ratio. The mixture was then subjected to reflux for 4 hours. The study examined the composite's swelling, diffusion, and network properties, which resulted in an increase in the rate of water sorption and urea adsorption.

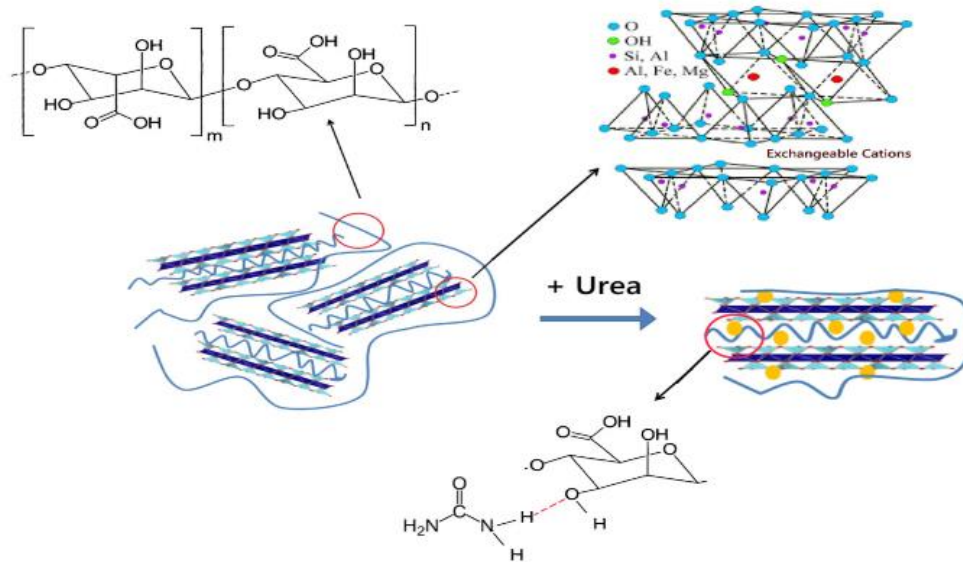


Figure 12. Illustration of saponite in alginate-urea. Reproduced from ref. [62] with permission from Elsevier B.V. Copyright 2019.

Wen *et al.* [63] used bentonite primarily comprised montmorillonite (MMT) to the fertilizers NaAlg-g-p(AA-co-AM)/urea. The data presented in Figure 13 for NaAlg-g-p(AA-co-AM)/Bentonite/urea showed a release percentage of 60.3% on the third day, indicating a more efficient slow release property compared to NaAlg-g-p(AA-co-AM)/urea. Bentonite, a very porous structure and a convoluted pathway, impeded the diffusion of nutrients within the medium. The user's text is already academic.

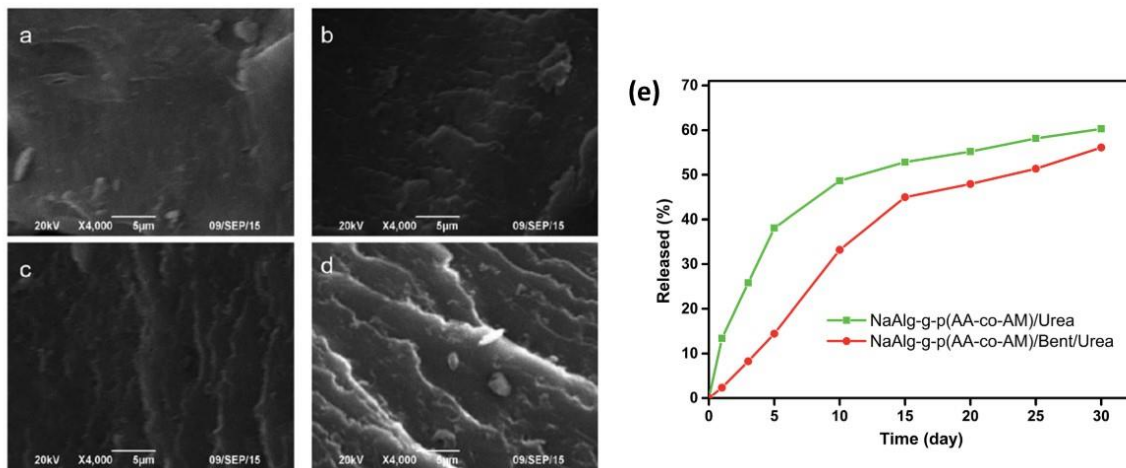


Figure 13. a-d) Na-Alg-urea SEM micrographs of NaAlg; **e)** fertilizer release. Reproduced from ref. [63] with permission from the Royal Society of Chemistry. Copyright 2016.

Based on the responses surface methodology (RSM), Babadi *et al.* [64] covered urea with gypsum-dolomite. The analysis reveals that the ideal circumstances for the coating process are as follows: a sprayed water concentration of 1.50%, a spray flow rate of 53 g/min, a coating percentage of 25%, a pan rotating speed of 16 rpm, and a particle size of 2.80 mm. Figure 14 was utilized to apply the response surface method in order to identify the optimal operating range that achieves an improved efficiency of 35%.

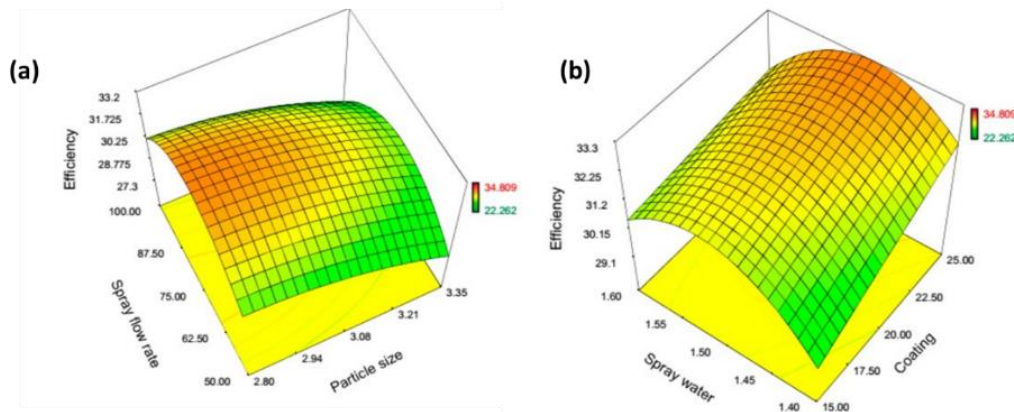


Figure 14. Response surface methodology of the efficiency with the effect of **a)** spray flow rate (g/min)-particle size (mm); **b)** spray flow rate (g/min)- coating percentage (%). Reproduced from ref. [64] with permission from the Multidisciplinary Digital Publishing Institute (MDPI). Copyright 2019.

6. Conclusion and Future Applications

Numerous studies have demonstrated the advantageous effects of composite material as a soil supplement. The distinctive characteristics of biochar offer an opportunity to enhance fertilizer efficiency by serving as a medium for nutrient loading. Conventional chemical fertilizers are associated with several limitations, including the quick leaching of nutrients, detrimental environmental degradation, and substantial economic costs. As a result, there has been a growing global interest in biochar-based slow-release fertilizers (SRFs). Presently, the predominant focus of scholarly investigations lies in the realm of synthesizing composite-based slow-release fertilizers (SRFs) that exhibit high efficacy. However, there exist issues pertaining to (i) more efficient SRFs synthesis, (ii) the long-term evaluation of practical implementation, and (iii) bioavailability and nutrient release assessment. However, existing research indicates that using composite-based soil remediation fertilizers (SRFs) is a feasible approach to enhancing sustainable agricultural practices.

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Conflicts of Interest

The authors declare no conflict of interest.

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