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Advances in Agricultural Technology: A Review of Slow-Release Nanofertilizers and Innovative Carriers

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ABSTRACT

Nanofertilizers represent a promising and innovative solution in modern agriculture, offering sustainability and efficiency to improve crop performance and optimize natural resource utilization. These fertilizers are distinguished by their nanometer-sized particles, facilitating better absorption and utilization by crops. A notable approach in nanofertilizer formulation is the controlled release of nutrients, ensuring a steady and gradual availability of essential elements to plants throughout their growth cycle. This approach curtails excessive fertilizer application, reduces leaching, minimizes negative environmental impact, and enhances nutrient utilization efficiency. Innovative carriers, in turn, play a fundamental role in the precise delivery of nutrients. Eco-friendly materials are being explored as sustainable alternatives to encapsulate the nutrients, ensuring they are available to plants when needed. This not only contributes to the preservation of natural resources but also reduces the negative environmental impacts associated with conventional agriculture. Therefore, this review article highlights promising advancements in agricultural technology, with a focus on the utilization of slow-release nanofertilizers and innovative carriers as sources of essential nutrients such as nitrogen, phosphorus, and potassium in agricultural practices, emphasizing the use of these technologies to promote environmental sustainability and agricultural efficiency.

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Slow release of nutrients; smart agriculture; sustainability in agriculture; nanofertilizers; innovative carriers; agricultural technology

Introduction

As the world's population continues to grow at an alarming rate, agricultural production is not keeping up. Crop yields are being further hindered by biotic and abiotic stresses, environmental contamination, and climate change, leading to nutrient deficiencies in plants ß (Pandey et al. 2017). To address these challenges, modern technology and strategies are needed to provide effective solutions to the global agricultural system. While chemical fertilizers and pesticides can increase crop production, they can also produce harmful residue that can affect human health, sustainability, and contaminate water, upsetting the delicate balance of the ecosystem (Zhang et al. 2018).

Plants require a balance of essential macronutrients and micronutrients for healthy growth and yield. If one of these components is missing, the plant may not be able to properly germinate from the

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seed (Madan et al. 2016). However, too much of any nutrient can be damaging to the plant. Finding the right balance of these nutrients to meet the needs of the plant's cellular processes is a difficult task (Duhan et al. 2017).

Nitrogen is present in a variety of chemical forms, including ammonium (NH_4^+), nitrite (NO_2^-), and nitrate (NO_3^-), as well as in the gaseous form. When fertilizer is applied to soil, up to 70% is used by the crop, while the remaining surplus nitrogen is discharged in the form of leachate to the soil and as harmful gases into the atmosphere. The ammonium ion is produced during the mineralization process, and is then converted into the nitrate ion which is more prone to leaching losses due to the negative charge of the soil clay particles. Unsafe ammonia and nitrous oxide are also sources of gaseous pollution. In order to reduce the risk of nitrogen losses, a controlled release fertilizer is needed to fulfill the crop's nitrogen requirements (Trenkel 2013).

Nanofertilizers are engineered nanomaterials (ENMs) that directly supply one or more essential nutrients to plants, or that boost the effectiveness, availability, and utilization of traditional fertilizers. It has been reported that between 1970 and 2008, the amount of fertilizer needed to produce one ton of grain increased by more than 300%. Furthermore, estimates suggest that global fertilizer usage increased from 182.8 Mt in 2013 to 186.7 Mt in 2014, and further to 199.4 Mt in 2017 (Yin, Wang, and Gilbertson 2018).

Nanotechnology-based delivery systems offer numerous advantages for agricultural applications. These systems are capable of providing sustained release of active compounds in the dosing interval between the minimum effective concentration and the maximum safe concentration, thus reducing the amount of active compounds needed for a biological response (Figure 1). Additionally, these delivery systems can decrease the risk of environmental contamination, energy consumption and labor costs, while also providing greater safety for agricultural crops and non-target organisms, such as pollinators (Fraceto Leonardo et al. 2016; Kremer Robert 2019; Shukla et al. 2019).

Till now 17 elements – Nitrogen (N), Phosphorus (P), Potassium (K), Hydrogen (H), Boron (B), Carbon (C), Oxygen (O), Magnesium (Mg), Sulfur (S), Chlorine (Cl), Calcium (Ca), Manganese (Mn),

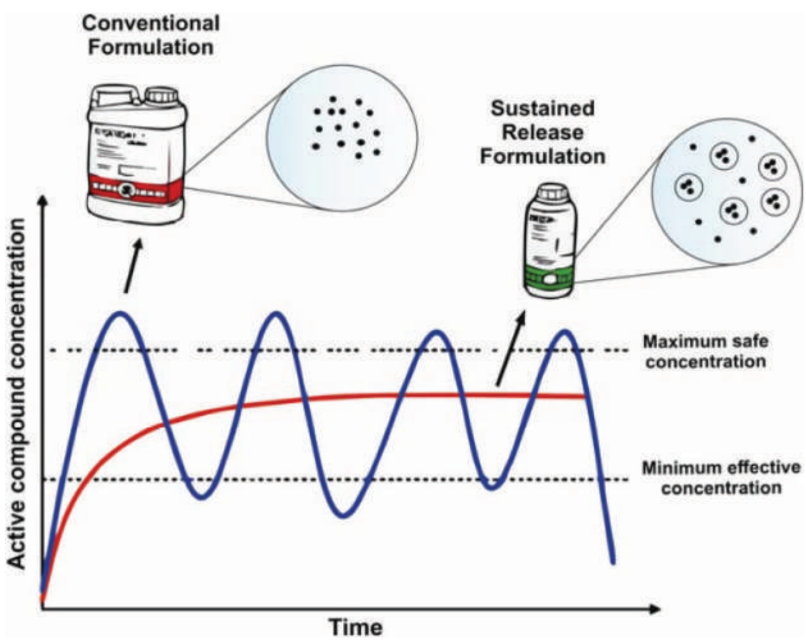

Figure 1. Schematic representation of a conventional system and a sustained release system for agricultural applications. The effectiveness and concentration of an active compound in a conventional system decreases as a function of time, requiring new applications. The sustained release system, however, maintains the concentration of the active compound in an effective range of action.

Iron (Fe), Nickel (Ni), Copper (Cu), Zinc (Zn), Molybdenum (Mo)-have been identified as essential nutrients for plant growth and development. Among them, nitrate, P, K and Mg are major essential elements needed by the plant. They cannot be absorbed directly from the atmosphere, but plants absorb them through their roots (Wang et al. 2016). It is known that micronutrients such as Cu, Mn, and Zn are critical for the activation of enzymes and the synthesis of biomolecules involved in plant defense. However, the efficacy of conventional fertilizer-micronutrient amendments is hindered by low nutrient bioavailability in neutral to alkaline soils and poor basipetal transport in plants (Elmer Wade and Jason 2016; Wang et al. 2012).

Tarafder et al. (2020) proposed a new formulation of a hybrid nanofertilizer (HNF) for slow and sustainable release of nutrients in both soil and water. The authors synthesized hydroxyapatite modified with urea and incorporated Cu, Fe, and Zn nanoparticles to enhance the efficiency of the proposed fertilizer. The results indicate that the slow-release nanofertilizer has the potential to gradually release the nutrients Ca^{2+}, PO_4^{3-}, NO^{2-}, NO^{3-}, Cu^{2+}, Fe^{2+}, and Zn^{2+}. This nanofertilizer was applied to A. esculentus plants and demonstrated maximum nutrient absorption efficiency, resulting in higher levels of productivity. Furthermore, it was observed that the nanofertilizer also improved the absorption of Cu^{2+}, Fe^{2+}, and Zn^{2+} nutrients compared to a commercial fertilizer in just a few days. These findings showcase the effectiveness of the slow-release technology and the utilization of the nanomaterial product, significantly enhancing nutrient absorption compared to conventional fertilizers.

In this context, we highlight numerous studies and applications of slow-release nanofertilizers and alternative carriers as sources of nutrients, which represent significant advancements in modern agriculture, with the potential to serve as an alternative to conventional agricultural practices. By incorporating these technologies, farmers can enhance the efficiency of N, P, and K utilization while simultaneously minimizing environmental impacts, thereby contributing to a more sustainable and productive agricultural system.

Search startegy

All articles and studies were identified based on ScienceDirect and Google Database searches dating from January 2010 to May 2023. The combination of keywords and phrases in relation to this review article, including "Nanofertilizers and Innovators," "Controlled Release," "Agriculture," "Slow Release," "Wall Materials" and "Nanomaterials." In total, 1,077 relevant articles were selected. After screening, 202 eligible studies were identified and included in this article.

Criteria of eligibility

Only journal articles focusing on nanofertilizers, wall materials, nanoencapsulation and controlled release advances to improve soil enrichment and optimize nutrient bioavailability were included in this study. Eighteen studies evaluated the main wall materials used for slow-release/controlled-release fertilizers and their influence on the efficiency of NPK availability to crops. Several studies focused on evaluating the properties, characteristics and efficiency of wall materials for formulating nanofertilizers, as well as their availability for the nutrients needed by crops and soils. Studies were found for chitosan (16 studies), sodium alginate (07 studies), starches and derivatives (12 studies), cellulose (7 studies), lignin (8 studies), biochar (10 studies), agricultural residues (8 studies), polydopamine (4 studies), nanozeolite (7 studies), nanohydroxypatite (14 studies), nanoclay (8 studies) and nanobiofertilizers (63 studies).

Nutrients

Macronutrients are the most essential for plant growth and development, while micronutrients are needed in smaller amounts, yet still very important for plants. When a deficiency of micronutrients occurs, it can weaken the plant's resistance to environmental stressors, leading to decreased crop yield and quality. Furthermore, micronutrients play a vital role in maintaining a balanced physiological state of plants and are often the limiting nutrient. Additionally, certain micronutrients are necessary cofactors for enzymatic reactions associated with various biochemical and cellular processes (Fageria, Baligar, and Clark 2002).

Macronutrients

By 2050, it is estimated that the global demand for macronutrient nanofertilizers, which provide plants with essential nutrients such as N, P, K, Ca, Mg, and S, will have increased to 263 Mt (Alexandratos and Bruinsma 2012; Chhipa 2017).

According to literature, conventional macronutrient (N, P, and K) fertilizers are inefficient and lead to considerable losses of resources (Zulfiqar et al. 2019). Overall macronutrient fertilizer ($P_2O_5 + N_2 + K_2O$) consumption is projected to increase from 175.5 million tons (Mt) to 263 Mt by 2050 globally. Furthermore, due to heavy application, these macronutrients are transported into surface and groundwater bodies and disrupt aquatic ecosystems, as well as threaten human health. Therefore, an environmentally friendly alternative is desperately needed to replace conventional macronutrient (N and P) fertilizers and to ensure sustainable food production. This alternative is nanofertilizers, which are highly effective and eco-friendly (Liu and Lal 2015).

N is an essential nutrient for plant growth, and its insufficiency is often the most important limiting factor for the yield. Urea is the most widely utilized type of nitrogen fertilizer globally due to its high percentage of nitrogen and its relatively cheap cost, as well as its straightforward method of application. However, urea has a number of troublesome traits, such as its high solubility, low thermal stability, and low molecular weight, which cause it to easily volatilize, runoff, and leach into the soil and aquatic ecosystems. These properties also make it difficult for urea to be fixed by soil particles, leading to a utilization rate of conventionally designed urea fertilizer of below 35% in developing nations, where large quantities of urea fertilizer are used (Ni et al. 2011; Ni, Liu, and Lü 2009; Trinh Thanh et al. 2015). Additionally, the leaching of fertilizers into water sources can lead to eutrophication of lakes and reservoirs, which can threaten ecosystems (Fernández-Escobar et al. 2004; Naz and Anwar Sulaiman 2016).

Kumar et al. (2022) developed a nitrogen and zinc nanofertilizer for growing wheat, millet and oilseeds. Their results were compared with applications of conventional chemical fertilizers and showed that the nanofertilizer corroborated with a yield increase of 5.35% in wheat, 24.24% in sesame and 4.2% in millet. These results show the efficacy of using nanofertilizers in the cultivation of various plants.

The sustainability of P in terms of its use as an inorganic fertilizer has been identified as a critical issue for future agricultural and environmental sustainability (Hasan et al. 2016). P is a vital component of the protoplasm and nucleus of cells that stimulates the growth and development of plants. Generally, only up to 20% of the standard P fertilizer applied to the soil is taken up by plants. This percentage is drastically reduced due to volatilization and leaching of nutrients. These losses through water eutrophication and the release of harmful emissions due to the hydrolysis of nutrients and the activity of microorganisms can lead to environmental pollution and health problems (Azeem et al. 2014). As a limited and highly sought-after resource, it is essential to find effective ways to produce and utilize phosphorus. The ongoing and persistent challenge in agricultural production is the efficient utilization of P nutrients (Li et al. 2018).

Recently, researchers have initiated investigations into the field of nanoformulations of hydroxyapatite (nHAP; $Ca_{10}(PO_4)_6(OH)_2$) as a carrier for other nutrients and as a phosphate fertilizer, in addition to its soil bioremediation properties (Priyam et al. 2022). The studies have shown that the slow-release nanofertilizer led to an increase in P levels in tomato crops, promoting more robust germination and growth without inducing stress in plants when applied to various soil types.

K is a key nutrient component for plant growth and plays an important role in current agricultural practices (Borges et al. 2017). As it is the most commonly found cation in plants, it is involved in all growth-related functions. K is largely obtained from evaporative minerals such as sylvite and carnallite, which are found in the earth. Soil total K (TK) can be obtained in four distinctive forms, as depicted in (Figure 2) (Vejan et al., 2021). A small fraction of water extractable K is readily available to plants. However, Nonex-K is slowly or only by chance available for uptake by plants. The importance of K in plant growth is reinforced by its involvement in various crucial enzymes, such as photosynthesis, transport of sugar, synthesis of proteins, and the metabolism of C and N (Marschner 2012). Additionally, K is essential for crop production yield and quality enhancement (Oosterhuis Derrick et al. 2014). In plants, K plays a key role in the regulation of osmotic pressure and the balance of anions and cations in the cytoplasm. Its high mobility can be seen in the regulation of stomatal opening and closing and cell elongation, amongst other essential physiological processes. Unfortunately, K deficiency is a global issue and can have devastating effects on agriculture, such as decreased yields and impaired growth, enzyme activation, water linkages and charge balances, and reduced stress resistance. To combat this, controlled-release K fertilizers have been developed to improve fertilizer efficiency and reduce the impacts of K deficiency (Du et al. 2019; Hu et al. 2017).

Mg is an important macronutrient for plants, and Nano Mg is considered more efficient than a conventional source. Delfani et al. (2014) found that the application of MgNPs (0.5 g L^{-1} of MgNPs) to black-eyed peas (Vigna unguiculata) farming reduced seed growth by 6% (from 216 g to 206 g in the control group). However, a combination of 0.5 g L^{-1} Mg NPs and Fe NPs increased seed growth by 7% (from 216 g to 232 g). The greatest seed growth (13.5%, from 216 g to 245 g) was found when 0.5 g L^{-1} Fe-based salt was used instead of Fe NPs (Delfani et al. 2014).

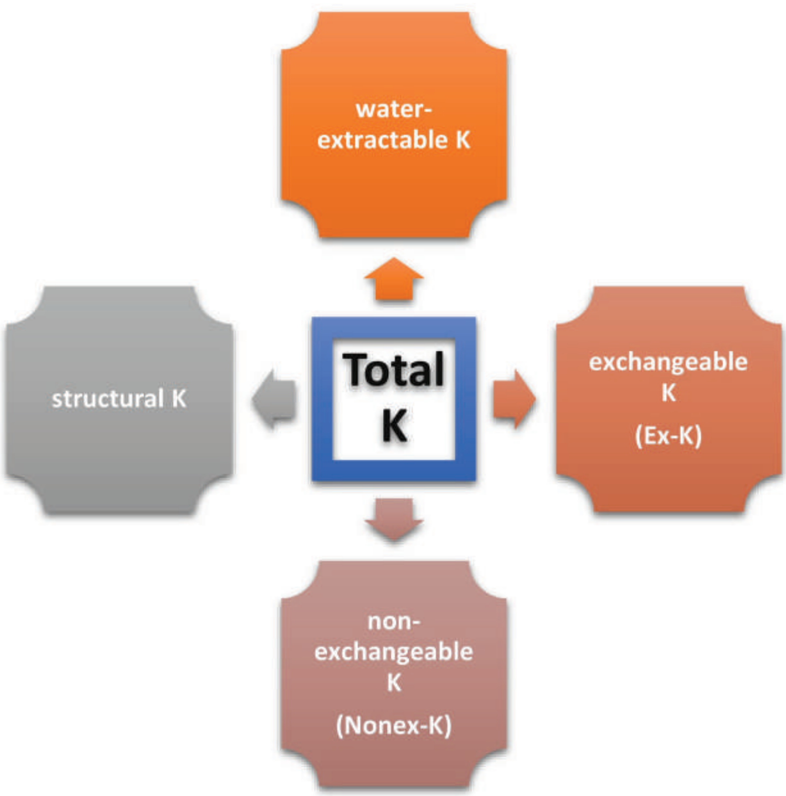

Figure 2. Different forms of soil total K (TK)- Water extractable K, Structural K, Exchangeable K and Non-exchangeable K.

Notably, over the past four decades, the nutrient use efficiency of the most important elements required by plants, including N, P, and K, has remained at a low average of 30–35%, 18–20%, and 35–40%, respectively (Manikandan and Subramanian 2016). This inefficiency in nutrient delivery to and use by plants results in the addition of excessive amounts, which can lead to environmental contamination from emissions, leaching, and run-off. Fortunately, several studies have reported that nano-enabled fertilizers have the potential to increase the efficiency of nutrient delivery to plants (Chhipa 2017). If this potential could be optimized, the economic and environmental benefits would be substantial (Manikandan and Subramanian 2016).

Micronutrients

Compared to macronutrients, micronutrient fertilizers provide essential nutrients to plants in relatively small amounts, usually no more than 10 mg kg^{-1} of soil. Nanoscale nutrient forms can increase the availability of these important elements, which then enhances the metabolism of plants, aiding in their growth, development, and nutritional quality (Dimkpa Christian and Prem 2018).

Micronutrients are essential to ensure the vitality of various metabolic processes in plants. These micronutrients, including Fe, Mn, Zn, Cu, Mo, and titanium dioxide (TiO_2), are usually added to NPK fertilizers as soluble salts at low rates for crop uptake. Although these nutrients are required in small amounts (≤100 ppm), their presence is necessary for healthy plant growth and development (Zulfiqar et al. 2019).

Fe is an essential micronutrient among micronutrient nanofertilizers which is necessary to ensure optimal plant growth, as reported by Hoagland et al. (1950). Generally, 1–5 mg L^{-1} of Fe is needed in the soil solution for expected performance. Mn is also required for the healthy growth of plants, and the optimal amount of Mn should be 0.5 mg L^{-1} in the soil solution (Pradhan et al. 2013). Zn is a mineral element which is essential for all plants for their regular growth and its other functions, such as activating enzymes, controlling the proliferation and differentiation of cells, and developing chloroplasts. However, too much Zn can be toxic, so optimization is necessary for its expected performance (Sturikova et al. 2018). Cu is needed in trace amounts for the normal growth of plants, but higher concentration can lead to toxicity. CuNPs-mediated fertilizers can provide fast release of nutrients and their ready availability for plants, making them more popular in agriculture since they can serve as both pesticides and fertilizers (Wang et al. 2020). Mo is also an important micronutrient for plants, which should be present in the soil solution in an amount of 0.01 mg/L to ensure regular metabolism (Taran et al. 2014).

Salama et al. (2022) carried out experiments to explore the impact of applying micronutrients in the nanoparticle form (MN-NPs) to common bean plants. Their findings indicate that the foliar application of micronutrients in the nanofertilizer form resulted in a substantial enhancement of vegetative growth parameters, the number of flowers per plant, photosynthetic pigments, and crop yield. Additionally, a concentration of 40 mg/L of MN-NPs was found to bring about improvements in vegetative growth, flowering, and production characteristics.

Overall, ENMs have the potential to significantly increase biomass or grain/seed yields, as demonstrated by studies evaluating both macro- and micro nutrient nano-enabled formulations. In some occasions, improved crop yields have been strongly correlated to the acquisition of nutrients from nanofertilizers, when compared to untreated controls or conventional nutrient-fertilizers. However, further research is necessary to gain a full understanding of the potential benefits of ENMs, including mechanistic evaluation of underlying processes and field scale studies under realistic conditions.

Slow release and controlled release

Controlled release fertilizers (CRFs) offer a variety of advantages over conventional fertilizers, including economic, environmental, and physiological benefits. However, there are also some drawbacks associated with them, and further research is needed to address these issues (Fertahi et al. 2021).

The environmental and health impacts of conventional fertilizer use are significant. Nearly 40–70% of nitrogen content is lost through leaching, mineralization, volatilization, gas emissions, soil erosion, and denitrification processes. Additionally, 80–90% of P is lost due to surface runoff and mineralization, and 50–70% of K is lost mainly through leaching and surface runoff. These losses lead to economic losses as well as detrimental environmental and health effects (Rop et al. 2018).

Nitrogen-based fertilizers can lead to contamination of groundwater through leaching and accumulation from agricultural activities. This poses an immediate danger to human health due to the deterioration of drinking water quality. Additionally, nitrate volatilization pollutes the air and causes adverse atmospheric effects, as well as dermal irritation and inhalation problems. Furthermore, phosphorus overflow can cause eutrophication in freshwater and estuaries, leading to algal blooms and water-related problems such as summer fish kills, foul odors, and unpalatable tastes in drinking water. Finally, excessive fertilizer use can have a detrimental impact on soil quality, including acidification, persistent organic pollutants, and heavy metal accumulation (Khan et al. 2017).

The use of Controlled Release Fertilizers (CRFs) has the potential to reduce nutrient losses, as well as to minimize the potential negative effects and the risk of environmental pollution described previously. However, despite their positive effects, CRFs also come with certain drawbacks which need to be addressed. The main problem with CRFs is their use of slowly or non-degradable materials, such as certain types of polymers. The slow degradation of these materials can lead to an accumulation of plastic residues, up to 50 kg/ha/yr, and 500 kg/ha can take almost 10 years to decompose to just 200 ppm of dry soil (Fertahi et al. 2021).

The agronomic effect of controlled-release fertilizers (CRFs) is multi-faceted. CRFs can improve plant growth conditions by slowly releasing nutrients to match the plant's needs, resulting in less osmotic stress or root and leaf burning caused by conventional fertilizers. Furthermore, CRFs have the potential to enhance soil quality, improve germination rates, reduce stalk breakage, and reduce disease infestation. Additionally, CRFs can increase nutrient availability, leading to higher protein levels in the plants and higher yields (Fertahi et al. 2021).

By using CRFs, farmers can experience cost savings in terms of the quantity of the fertilizer needed and the labor, time, and energy in applying the fertilizer. A single application of CRFs can meet crop nutrient demands for an entire season, thus reducing the application frequency and providing savings in regard to the spreading costs (Trenkel 2013). Additionally, the storage and handling of CRFs are also more convenient. However, the manufacturing cost of most coated or encapsulated CRFs is still considerably greater than that of conventional mineral fertilizers due to the price of the materials and the process, although these expenses can largely be compensated by the gains mentioned above (Fertahi et al. 2021).

A fertilizer can be considered to be slow-release if the nutrient or nutrients declared as such meet three criteria in soil under specific conditions, including a temperature of 25°C, as stated by (Trenkel 2013).

– No more than 15% (m/m) released in 24 h.
– No more than 75% (m/m) released in 28 days;
– At least 75% (m/m) released at the stated release time.

The effectiveness of slow-release fertilizer is dependent on numerous factors, such as the chemical and physical properties of the coating material, atmospheric temperature, soil moisture, agricultural environment, farming methods, and more. To understand the pattern of nutrient discharge in soil, it is theoretically simple to judge the fertilizer efficiency; however, due to the complexity of the parameters that affect its performance, it is difficult to visualize the slow release of nutrients. Beig et al. (2020) have explored the various factors that influence the performance of slow-release fertilizers.

Atmospheric temperature and humidity are very important variables that influence the release of N from fertilizer, specifically slow release fertilizer. High temperatures accompanied by humid atmospheric conditions enhance the nitrogen release from coated urea. The N release process is principally driven by water, which transports nitrogen from the fertilizer-polymer boundary to the polymer soil boundary. The rate and mechanism of this process are determined by solid dispersion/inflammation, deterioration of urea coating, and rupture of coating, water penetration, and dissolution (Beig et al. 2020).

The multi-stage diffusion model developed by explains the release rate and process of nutrients from polymer coated fertilizer. When the polymer coated fertilizer is applied to soil and irrigated, the water penetrates into the central part of the fertilizer granule, resulting in condensation and gradual release of nutrients. Depending on the osmotic pressure, two possible mechanisms occur. If the osmotic pressure is greater than the resistance of the coating, the material coating cracks and the entire nutrient gets released quickly, referred to as the "failure mechanism" or "catastrophic release." If the film resistance is strong enough to withstand the built-up osmotic pressure, the nutrient nitrogen is slowly released through diffusion, driven by concentration or pressure difference, or both. This is known as the "diffusion mechanism." Fragile S or modified coatings usually follow the failure mechanism, while polymer coated urea fertilizer generally follows the diffusion process for nutrient discharge (Beig et al. 2020).

Wall materials

It is widely recognized that the accumulation of NPK, Ca, Mg and S from traditional fertilizer sources can be detrimental to agroecosystems. Run-off of these macronutrients can pollute bodies of water, potentially resulting in eutrophication and the degradation of aquatic ecosystems. Using engineered nanomaterials (ENMs) as alternative sources for these nutrients may reduce environmental impacts, as overall usage of these elements would be significantly decreased. This benefit is complemented by improved crop productivity due to more efficient delivery, better accessibility, and more focused temporal and spatial release (Adisa Ishaq et al. 2019).

Nanomaterials like ZnO (Zulfiqar et al. 2019), CuO (Y. Wang et al. 2020), Fe (Li et al. 2020), SiO_2 (Kumaraswamy et al. 2021), TiO_2 (Zulfiqar et al. 2019), AgNPs (Younis, Abdel-Aziz, and Heikal 2019), MWCNTs (Usman et al. 2020), Al_2O_3 (Osman et al. 2020), etc. have been used to ensure slow and controlled delivery of fertilizers, promote good seed germination, improve water absorption, enhance biomass accumulation, mitigate the effects of toxins on plant growth and photosynthesis processes (Du et al. 2019). The potential application of nanomaterials on plant root progress is also being explored, with focus on reducing the bio-concentration of toxic nutrients and strengthening root nodulation. A recent trend in agriculture is the encapsulation of microorganisms with nanomaterials, which has been found to improve plant root health by reducing the leaching and volatilization of nutrients in the root zone (Pallavi et al. 2016).

A review by Rodrigues Sónia et al. (2017) identified various promising opportunities for applying nanotechnology to improve sustainable agri-food systems. These opportunities include using nanotechnology to improve controlled release and target delivery of agrochemicals (e.g., nanofertilizers and nanopesticides) to control pathogens and increase food safety and security, as well as creating sensors to assess specific conditions or analytes of interest in plant systems. These applications offer a promising platform that makes ENMs a preferable alternative to traditional fertilizers and pesticides. Furthermore, ENMs can be integrated with conventional fertilizers and pesticides to improve their effectiveness, either by being incorporated in bulk formulations or being the only active ingredient.

ENMs such as silver (Ag), cerium (Ce), Cu, Mn, titanium (Ti), and Zn are the most commonly studied materials in plant growth and disease management. Various organic-based biopolymeric nanoparticles, such as chitosan and β-D-glycan, have been used alone or combined with other ENMs to improve plant growth and/or combat plant diseases. Additionally, silica, Ag, Al_2O_3, TiO, and ZnO have been demonstrated to have insecticidal activity, while Ag, Cu, CuO, Fe, Mn, and Zn have shown promise as herbicides. However, the results of these studies may be affected by the dose, plant species, application mode, environmental conditions, and experimental/exposure designs (Adisa Ishaq et al. 2019).

The high surface area and penetrability of ENMs makes them potentially more efficient than conventional fertilizers in terms of nutrient use. This can be seen through the controlled or slow release of macronutrients such as N which has been achieved from materials like nano-enabled urea-coated zeolite chips and urea-modified hydroxyapatite (HA) (Chhipa 2017; Kottegoda et al. 2017).

Several nanofertilizers based on NPK, such as nanohydroxyapatite, urea-modified zeolites, and mesoporous silica nanomaterials, have been investigated for their ability to provide a controlled or slow release of fertilizer (Zulfiqar et al. 2019).

The eutrophication potential of P nanomaterials (NMs) in acidic and alkaline soils must be evaluated to provide insight into their applicability in actual soils. Hydroxyapatite NMs have previously been reported to increase seed productivity (20%) and plant growth (33%) of Glycine max compared to traditional P fertilizer, in an inert medium. Thus, these NMs could be promising for increasing crop yields in agricultural settings (Liu and Lal 2014).

The influence of ENM treatment on nutrient acquisition has been reported to have analogous effects to those of vegetative and reproductive growth. Nanocomposites of ZnO, CuO, and B_2O_3 were found to significantly increase the uptake of N, K, Zn, and B under drought stress, compared to untreated controls. This suggests that fortifying N and K macronutrient fertilizers with nano-scale micronutrients can increase overall nutrient use efficiency, potentially mitigating the effect of N loss to greenhouse gas production (Adisa Ishaq et al. 2019).

ENMs that are not classified as plant nutrients have been found to have a positive impact on plants, such as carbon nanotubes (CNTs), CeO_2, SiO_2, and Titanium dioxide (TiO_2). While these materials do not provide nutrition, they have been shown to stimulate growth and increase crop yield. Studies have found positive results in plants treated with high concentrations of ENMs (>500 mg L^{-1}) (Delfani et al. 2014; Dimkpa Christian et al. 2018; Rui et al. 2016; Salem Nidá et al. 2015). One of the advantages of using ENMs over traditional fertilizers is cost savings. However, if large quantities of ENMs are needed to achieve the desired results, the cost-savings will be negated and their use in agriculture will be unlikely. Thus, studies on the effects of ENMs on plants should include a cost-benefit analysis, as discussed by Dimkpa Christian and Prem (2018).

TiO_2 nanomaterials have emerged as an effective and sustainable solution for environmental issues in agriculture. TiO_2 is regarded as an ideal photocatalytic material due to its photoactivity, chemical stability, tunable hydrophilicity, and biocompatibility. According to Rodríguez-González, Terashima, and Fujishima (2019), TiO_2 nanomaterials (TiO_2 NPs) offer advantages over conventional metallic nanomaterials, which are unbalanced in water, and carbon-based nanomaterials that are readily absorbed. The results of their review revealed that TiO_2 NPs did not have a significant impact on the germination of several common crops such as rice, lettuce, radish, cucumber, tomato, and pea, although root elongation was observed at a lower dose (0.5 g/kg). Furthermore, application of TiO_2 NPs at the lower dose was found to increase barley production, as well as the concentrations of amino acids, Ca, Mg, and Zn in the grain.

Recently, the use of engineered nanomaterials (ENMs) in plant disease management and soil fertilization has gained traction, with various reports suggesting significant potential. For instance, a number of ENMs have been reported to improve growth, enhance nutrient use efficiency, and suppress diseases in plants in both greenhouse experiments and a small number of field trials (Adisa Ishaq et al. 2019).

Since 2000, the Web of Science database has indexed 795 research articles using the keywords "Polymer coated fertilizers", "Controlled release fertilizers" and "Slow release fertilizers" in title. According to the collected data (Figure 3(a)) and the evaluation of keywords in terms of frequency, the keyword "Controlled release fertilizers" was found to have the highest occurrence frequency of 389, accounting for 48.2% of all global publications in this field. This was followed by "Slow release fertilizers" with 379 (47.7%) and then the keyword "Polymer coated fertilizers" with 33 (4.1%). Additionally, the number of publications related to this field has grown exponentially, from 14 in 2000 to 98 in 2018 (Figure 3(b)). This shows the increasing interest in the research of this topic (Fertahi et al. 2021).

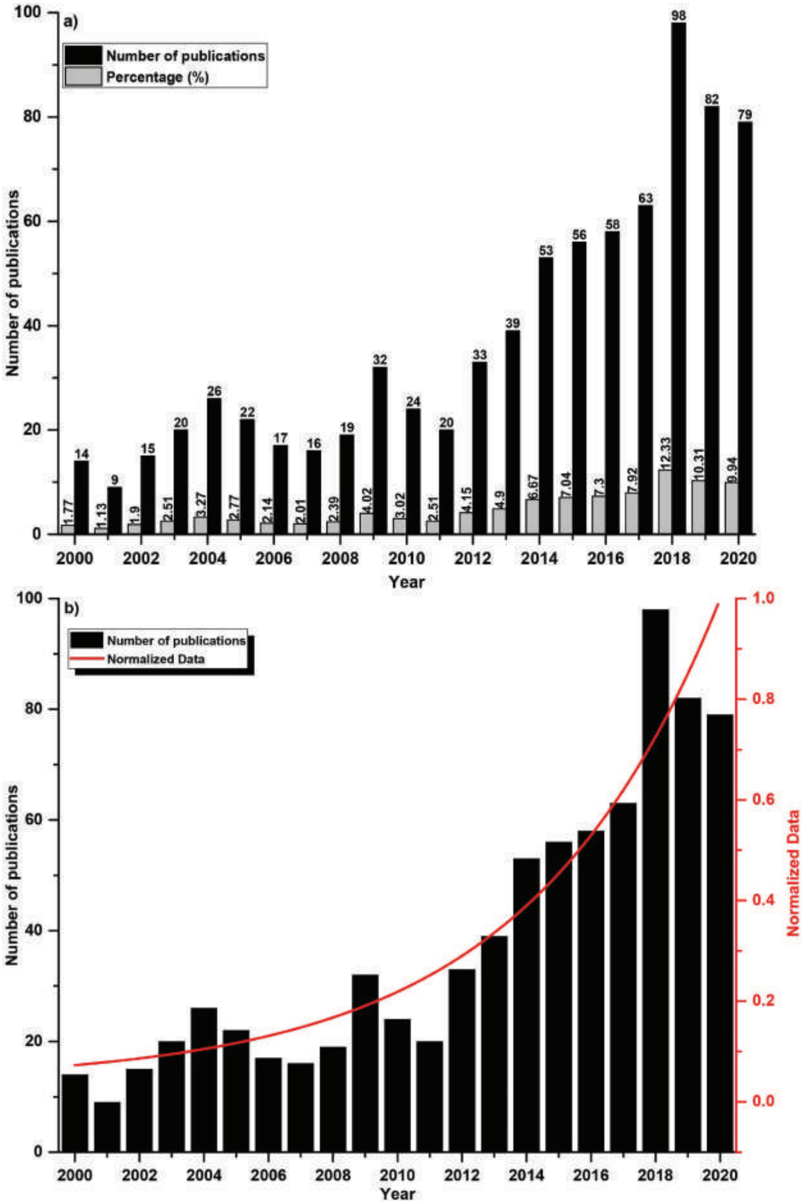

Figure 3. a) number of papers published between 2000 and 2020 involving keywords "polymer coated fertilizers" or "controlled release fertilizers" or "slow release fertilizers", b) normalized data by the total number of articles published in each analyzed year.

Over the years, the use of nanoparticles in controlled-release fertilizers (CRFs) has been further refined to improve stability, release mechanism, and nutrient storage. To address the limitations of the hydrophilic nature of previously formulated biomaterial-coated CRFs, scientists introduced a superhydrophobic CRF coated with bio-based polyurethane (BPU), modified further with organosilicon (OS) and nano-silica (NS) (Qiao et al. 2016). In addition to polymeric nanoparticles, other polymers, non-nanostructured, could also be used as a binding unit or as a second tier protective layer for nano-enabled fertilizers (Ahmad, Fernando, and Uzir 2015; Messa and Faez 2020).

Chitosan

Chitosan is a naturally-occurring, nontoxic and degradable polysaccharide derived from the partial deacetylation of chitin – a major component of crustaceous water animals such as crabs and shrimp. Its abundance in nature and its degradation properties make it an ideal resource for a variety of applications, including agriculture (Harish Prashanth and Tharanathan 2007; Li et al. 1992; Perez Jonas and Nora 2016; Rinaudo 2006; Wang et al. 2014; Xing et al. 2015). Moreover, its nonpolluting quality makes it particularly suited for use in environmental friendly fertilizers (EFFs) (Jamnongkan and Kaewpirom 2010; Rattanamanee et al. 2015; Sabadini Rodrigo, Virginia, and Pawlicka 2015).

Chitosan-coated nitrogen, phosphorus and potassium compound fertilizer has been developed as an environmentally friendly and cost-effective alternative to traditional fertilizers. The fertilizer cores contain N 8.06%, P 8.14%, and K 7.98%. The percentages released were 79, 62, and 69% for N, P, and K on the 30th days, respectively. The compound fertilizer has water-holding and water-retention properties in soil, which enable it to slowly release nutrients over time. However, the chitosan was coated on the fertilizer cores using epoxy dissolved in acetone, which may cause environmental pollution due to the emissions of organic solvents.

Another example of a chitosan-based fertilizer is the chitosan-montmorillonite clay microsphere fertilizer, which was created using a coagulation method and added to KNO_3 fertilizer solutions to obtain potassium-containing fertilizers. The montmorillonite clay was included to enhance potassium adsorption due to its rough and porous surface. Additionally, the clay is inexpensive, easily accessible, and environmentally friendly. The fertilizers were applied to the soil, and the potassium release was monitored using time-domain reflectometry (TDR). This method revealed a higher fertilizer release during the first three days, which was attributed to the KNO_3 on the microsphere's outer layers. Subsequently, the potassium concentration decreased until a constant value was achieved. The use of TDR to determine fertilizer releases provides a useful technique for soil application. Nevertheless, further research is necessary to assess the sustainability of the fertilizer delivery system, as the environmental effects were not examined (Santos et al. 2015).

Furthermore, researches into the use of chitosan as a growth enhancer, antimicrobial, and agrochemical (micronutrient and pesticide) delivery system for plants is increasing. Its potential to act as a natural, biodegradable, and affordable cationic biopolymer is being explored. Though chitosan has been noted for its antimicrobial activities in bulk form, its insolubility in aqueous media hinders its homogenous dispersibility when applied to plants, reducing its efficacy (Malerba and Cerana 2016).

Chitosan is often treated in acidic aqueous media and dialyzed to make it more spreadable on plant surfaces; however, this process can lead to increased toxicity on target organisms, increasing the inhibitory effects of its bulk form. In contrast, Chitosan Nanoparticles (CNMs) are much more water-soluble and have a higher positive surface charge than bulk chitosan (Adisa Ishaq et al. 2019).

The positive surface charge of CNMs increases their affinity for biological membranes, making them more reactive with biological systems than bulk chitosan. This increased affinity for both organic and inorganic materials, particularly metals, micronutrients, and macronutrients like nitrogen, can lead to enhanced seed germination, improved plant growth, increased nutrient uptake, increased photosynthetic rate, and increased crop yield (Kashyap, Xiang, and Heiden 2015; Kumaraswamy et al. 2018).

The encapsulation of active chemicals in nanoparticles has been shown to promote the efficacy of chemical compounds, reducing volatilization, toxicity, and environmental pollution (Beig et al. 2020). Chitosan is an ideal polymer for use as a fertilizer carrier/coating due to its abundance, biocompatibility, low cost, biodegradability, and compatibility with agricultural practices. Additionally, it has sorbent and antibacterial properties, making it a reliable and efficient material for fertilizer coatings (Kusumastuti et al. 2019).

Sodium alginate

Sodium alginate (SA) is a linear polysaccharide derived from brown seaweed that is composed of 1–4 linked α-L-guluronic and β-D-mannuronic acid moieties. It can be ionically crosslinked with the addition of Ca_2^+ in an aqueous solution, which makes it suitable for use as a controlled release formulation of fertilizer (Guo et al. 2006; Wu et al. 2011). However, the sodium alginate matrix has a weak mechanical strength and can be easily destroyed in the presence of monovalent cations, leading to a burst release of nutrients rather than the desired controlled-release (Kenawy and Sakran 1996; López, Deladino, and Martino 2013).

To address the issue of fertilizer loss Wang et al. (2012), proposed a method in which urea granules are coated with a k-carrageenan-sodium alginate (kC-SA) complex and cross-linked kC-g-poly(acrylic acid)/Celite (kC-g-PAA/Celite) superabsorbent. The kC-SA complex is formed by dropping kC and SA aqueous solutions into potassium chloride and calcium chloride mixed solutions. By introducing kC into the SA hydrogel, the mechanical properties of the hydrogel were improved and its brittleness reduced. The kC-g-PAA/Celite superabsorbent was then applied to the surface of the granules while rotating, reducing the loss of fertilizer. This product contained 22.6% nitrogen and exhibited slow-release behavior, with 94.2% of the nitrogen being released after incubation in soil for 25 days (Pourjavadi, Zeidabadi, and Sh 2010).

This study is similar to the one conducted by He et al. (2015). Raoultella planticola Rs-2 was encapsulated in sodium bentonite and alginate composites and the encapsulation efficiency was almost 100%. The bentonite increased the viscosity and mechanical strength of the alginate hydrogels and regulated the release of the bacteria over a period of 30 days. The study showed that the presence of bentonite minimized the burst release of bacteria and allowed for a sustained release over time. These results demonstrate the potential of bentonite and alginate composites for the encapsulation and slow-release of bacteria.

Starch and its derivatives

Starch is a polysaccharide composed of numerous monosaccharides (glucose) molecules linked together by α-1,4- and/or α-1,6-glycosidic bonds. It is the most abundant storage polysaccharide found in plants and provides the main source of carbohydrates in diets. Starch's abundance of hydroxy groups allows for easy modification, making it a desirable, cost-effective, and environmental-friendly component for the production of EFFs (Ge et al. 2002; Jin et al. 2013; Qiao et al. 2016; Zhong et al. 2013).

Two types of starch derivatives, starch acetate and carboxymethyl starch, have been utilized to produce double-coated fertilizers (Lü et al. 2014). First, urea and attapulgite clay were mixed and used as a core. Then, starch acetate with a high-substitution degree was synthesized and applied as a hydrophobic inner coating. To complete the outer coating, carboxymethyl starch and xanthan gum were blended to form absorbent materials. The double-coated fertilizers demonstrated an equilibrium release of nitrogen within 20 days. Additionally, natural polysaccharides were included to enhance biodegradability and environmental protection. The nutrient-controlled release behavior was observed to follow a sigmoidal pattern (initial slower release rate followed by consistent increases).

Starch-based graft polymers were synthesized and applied as fertilizer-coating materials. For instance, $K_2S_2O_8$ was combined with gelatinized starch at 80 °C to create $K_2S_2O_8$ modified starch, which initiated the polymerization of natural rubber to form a natural rubber-g-starch graft polymer (Riyajan, Sasithornsonti, and Phinyocheep 2012). Subsequently, urea granules were immersed in the graft polymer blend to develop coated fertilizers. The graft polymer had a core – shell structure, with the hydrophobic natural rubber as the core and the hydrophilic grafted starch as the shell. Consequently, urea particles were encapsulated in the starch layer and the hydrophobic natural rubber core formed a barrier to decrease nitrogen releases.

Cellulose and its derivatives

Cellulose, a polysaccharide composed of a linear chain of β (1–4) linked D-glucose units, is the most abundant biopolymer on earth. Multiple hydroxyl groups on the glucose units can be partially or fully reacted with various reagents to create derivatives such as cellulose ethers and cellulose esters (Siró and Plackett 2010). Recently, application of cellulose and its derivatives as fertilizer coatings has gained attention due to their renewability, biodegradability, and film-forming abilities (Bajpai, Swarnkar, and Ahuja 2015; Bortolin et al. 2013; Davidson Drew, Mohit, and Frank 2013; Essawy Hisham et al. 2016; Li et al. 2015, 2016).

Lignin

Lignin is a copolymer of three phenylpropane monomers: sinapyl alcohol, coniferyl alcohol, and para-coumaryl alcohol (Pandey and Kim 2011). It is produced as a by-product of chemical pulping and lignocellulosic biomass-based ethanol production (Zakzeski et al. 2010), and is the second most abundant naturally occurring biopolymer after cellulose (Chowdhury Mohammad 2014). Lignin is a cost-effective, biocompatible, and renewable resource from plant sources, and has numerous applications in agriculture (García Ma et al. 1996; Mulder et al. 2011; O'Hara et al. 2012; Sipponen et al. 2017).

Four types of commercially available lignin have been used to coat urea granules, including soda flax lignin (Bioplast, Granit, Switzerland), softwood kraft (Indulin AT, Mead Westvaco, USA) and two lignosulfonates (Wafex P and Borresperce, Borregaard/lignotech, Sweden) (Mulder et al. 2011). Alkenyl succinic anhydride (ASA) was utilized to crosslink the lignin, resulting in granules with a smooth surface and a low number of pinholes. However, the urea was completely released within 1 hour in all formulations.

Lignin was modified using isocyanate-terminated polyurethane ionomers (IPUI) to form an acetic acid lignin-based hydrogel that was used to coat an ammonium sulfate fertilizer core. Controlled-release behavior was observed when compared to the uncoated ammonium sulfate, with increasing release as the mass ratio of AAL to IPUI increased from 0% to 35% (Peng and Chen 2011).

Biochar

Biochar is a form of carbon-rich material created through the thermal pyrolysis process of agricultural residues and other lignocellulosic biomass at moderately high temperatures (González et al. 2015). In addition to its potential as a biofertilizer, biochar has been found to have numerous positive environmental benefits, such as greater agricultural profitability, decreased eutrophication risk, carbon sequestration from the atmosphere, and land restoration. These effects have made biochar increasingly attractive to both the agricultural and environmental communities (Cai et al. 2016; Yao et al. 2013).

It is essential for CRF to have an effective nutrient loading capacity to guarantee optimal storage and utilization of nutrients. The polymers making up the CRF walls are critical in exhibiting properties that could result in efficient nutrient loading capacity. For example, CRF can use biochar as part of its construction materials to create nutrient encapsulation walls. Biochar has excellent adsorption of nutrient ions such as potassium, phosphate, nitrate, and ammonium through its various functional groups, including lactone, carboxylic, chromene, hydroxyl, and ketone groups. These functional groups on the biochar lead to effective loading of nutrients and decreased soil nutrient loss (Kammann Claudia et al. 2015; Qian et al. 2014; Schmidt et al. 2015).

A recent study by Wen et al. (2017) developed biochar-based slow-release nitrogen fertilizers (BSRFs) composed of a polymer matrix of cotton stalks (CSs), acrylic acid (AA), 2-acrylamide-2-methylpropanesulfonic acid (AMPS), and bentonite (bent) into NH_4^+ loaded biochar (N-BC). These BSRFs showed high nitrogen-use efficiency (64.27%), low nitrogen migrate-to-surface-loss amounts (7.4%), and low nitrogen-leaching-loss amounts (10.3%). In addition, they successfully reduced the nitrogen-release rate (69.8% of nitrogen was released after 30 days) and effectively promoted cotton plant growth.

A controlled release fertilizer biochar, containing urea as an N source and impregnated onto biochar in a batch reactor and encapsulated with polysaccharide-based polymers including sodium alginate, cellulose acetate and ethyl cellulose, may be considered an example of biochar-based EFFs (González et al. 2015). Although the leaching potential of the fertilizer-biochar was investigated in soil columns with and without wheat, the crop yield was negatively affected by the developed formulations in comparison to commercial N-CRF (ESN).

A waterborne polyacrylate emulsion consisting of methyl methacrylate, butyl acrylate, methyl acrylic acid, and a crosslinker aziridine was modified with biochar (1%, w/w) to create a membrane coating for use in fertilizer-controlled release. The effect of the membranes on the soil bacterial community profiles was then determined by Biolog EcoPlates and polymerase chain reaction-denaturing gradient gel electrophoresis. After being incubated in paddy soil for 12 months, the results showed that there was no significant change in the composition diversity of the dominant bacterial community. However, the activity and functional diversity of soil culturable microbial community decreased during the early stages of incubation, due to the release of small amounts of soluble organic materials. This decreased activity recovered after 12 months, indicating that waterborne polyacrylate materials are environmentally friendly and have potential for the development of coated controlled-release fertilizers (Zhou et al. 2015).

Recently, a novel and innovative biochar-based controlled-release nitrogen fertilizer (CRF) was synthesized hydrothermally and has superior nutrient release characteristics (Liu Xiaofeng, Jia, and You 2019). Analysis of XRD and FTIR results showed that urea particles were successfully loaded into the channels and pores of the biochar. The urea loading capacity of the biochar was complemented with the nutrient retention capability provided by the swelling of bentonite, which halts nutrient dissolution. Previously, a diammonium phosphate (DAP) loaded CRF was synthesized using nano-clay/polymer composite (NCPC) that had undergone a series of organic modifications. The capability of loading 14 g DAP per unit weight of NCPC enhanced the efficiency of phosphorus fertilizer application. Similarly, clay was incorporated into the polymeric network to limit water permeability and nutrient release for urea and phosphorus fertilizer, respectively. These promising properties reduce production costs and improve nutrient utilization efficiency for essential macronutrients (Verma et al. 2016).

In 2021, a team of researchers presented a phosphate CRF with a unique dual mechanism involving the combined use of composite biochar and biofilm, demonstrating a maximum PO_4^{3-} loading capacity of 130 mg per g of composite biochar as determined by adsorption tests (An et al. 2021). Biochar is increasingly being employed as an efficient method for storing and loading nutrients in CRF synthesis due to its abundance of pores, high specific surface area, and availability of natural raw materials. Additionally, its traits as a soil conditioner and water-retainer are highly beneficial for its application in this field (Bong Cassendra et al. 2020).

Agricultural residues

Agricultural residues, such as wheat straw and corn stover, are abundant, cheap, biodegradable, and renewable (Geng and Henderson 2012; Pittman Charles et al. 2012). Comprised of cellulose, hemicellulose, and lignin, these by-products of crop production can provide organic matter and improve soil fertility after degradation in soil (Johnson Jane et al. 2010). Unfortunately, approximately half of these residues are disposed of by discarding and burning, leading to severe environmental pollution (Bhatnagar and Sillanpää 2010). To mitigate this pollution and improve soil fertility, agricultural residues have been utilized in EFFs (Holkar Chandrakant et al. 2016; Li et al. 2015; Ma et al. 2011; Schneider, Deladino, and Zaritzky 2016; Xia, Xu, and Yang 2017; Yang et al. 2013).

Zhang et al. (2014) developed a slow-release urea fertilizer (SRUF) made from mulberry branch-g-poly(acrylic acid-co-acrylamide) superabsorbent was developed to be eco-friendly.

This SRUF improved the water-retention of the soil compared to the control without SRUF. After 25 days, the water-retention ratio of the soil (100 g) with 0.5 g of SRUF stayed at 7.2 wt %, whereas the control had a water-retention ratio of 2.0 wt % after 10 days. However, the urea released in both deionized water and soil had high release rates, with 85 wt % of the urea released within 130 minutes in the water and nearly 100% of the urea released after 10 days of incubation in the soil. This may be due to the blending of the urea with the superabsorbents during preparation, as opposed to coating the urea with the superabsorbents. The fast-absorbing rate of the superabsorbents resulted in a significant release of urea from the fertilizer.

A coated fertilizer with a core/shell structure based on modified wheat straw was synthesized by Xie et al. (2011). The core of the fertilizer was comprised of urea and an attapulgite and alginate matrix, while the shell was a chemically modified wheat straw-g-poly(acrylic acid)/attapulgite (CMWS-g-PAA/APT) superabsorbent containing urea and borax which provided N and B respectively. The N and B contents of the product were determined using an ammonia-selective electrode and inductively coupled plasma, yielding values of 23.3% and 0.65%, respectively. Furthermore, the product was demonstrated to have both slow-release and water-retention capabilities.

Therefore, the use of agricultural residues for the development of nanofertilizers represents a promising and sustainable approach to enhance nutrient efficiency in agricultural practices. This strategy not only enables the recycling of waste materials, reducing waste and environmental impact but also offers the potential to improve crop growth and increase food production more efficiently.

Polydopamine (pdop)

Inspired by mussels, which have a strong ability to attach to a variety of surfaces even in wet environments, scientists have discovered that polydopamine can be easily applied to virtually all types of organic and inorganic substrates. This makes polydopamine a primary pigment in naturally occurring melanin (eumelanin), and has led to its widespread use as a coating material in a variety of applications (Liu and Lal 2014; Xu et al. 2017).

Jia et al. (2013) demonstrated that double copper potassium pyrophosphate trihydrate could be coated with a Pdop film through spontaneous oxidative polymerization of dopamine. Subsequent studies revealed that slow release behavior of the nutrients was observed in both water and soil, and that the release rate of these nutrients can be adjusted by employing a multistep deposition technique. As the number of deposition cycles increases, the thickness of the Pdop coating increases and the release rate of the nutrients trapped in the Pdop film decreases.

A double-copper potassium pyrophosphate trihydrate fertilizer core was designed to provide three essential nutrients (P, K, and Cu) with pH-response and water-retention properties. A Pdop layer was then deposited on the fertilizer core, followed by the synthesis of a Pdop-based initiator on the surface of the core and the employment of surface-initiated (SI)-ATRP technique to graft poly(acrylic acid) on the Pdop layer. The result was a "crosslinked coating-graft-polymer brush" structure which exhibited pH-responsive controlled release behavior. P and Cu exhibited a slower release rate in the acid/neutral solution and a faster rate in the basic solution, while the opposite trend was observed for P. This was attributed to the charged/uncharged PAA layer, which generated a negatively charged layer in the basic solution and excluded anions ($P_2O_7{}^{4+}$) but allowed cations (K^+ and Cu^{2+} $U_2^+U_2^+$) to pass. At a low pH, the layer remained uncharged and served as a hindrance to reduce nutrient releases (Ma et al. 2013).

The researchers of Ma et al. (2013) grafted poly(N-isopropylacrylamide) onto the Pdop layer through the SI-ATRP technique to develop a thermoresponsive release fertilizer. Nutrient release experiments were conducted at 25°C and 37°C. The results revealed that the lower critical solution temperature (LCST) of 25°C saw a higher nutrient release rate than 37°C. This was attributed to the PNIPAm layer's thermal switch behavior, where the stretching of PNIPAm chains at 25°C enabled the permeability of nutrients, whereas the collapse of PNIPAm chains at 37°C hindered the permeability of nutrients, thus slowing down the release rate.

A "smart" fertilizer with poly(N,N-dimethylaminoethyl methacry-late) (PDMAEMA) grafting from Pdop-coated ammonium zinc phosphate was developed by Feng et al. (2015) to exhibit temperature- and pH-responsive behavior according to the ambient environment. In an acidic pH (below the pKa of PDMAEMA), the nutrient-release rate accelerated due to the complete stretching of the PDMAEMA brushes. In a medium pH, above the pKa of PDMAEMA, the brushes gradually shrank to hinder nutrient releases. In addition, the nutrient-release rate was fast at temperatures below the LCST of PDMAEMA in basic medium (pH above pKa of DMAEMA), leading to a high permeability of nutrients. However, at higher temperatures, such as at noon or in summer, excessive nutrient release decreased, thus preventing damage to plant roots. This "smart" fertilizer will improve nutrient availability, even when environmental conditions (temperature and pH) fluctuate.

The ability of polydopamine to adhere to surfaces, encapsulate nutrients, and release them in a controlled manner makes it an ideal candidate for optimizing the use of fertilizers in agricultural practices. Furthermore, this approach can contribute to reducing the excess leaching of nutrients that harms aquatic ecosystems. As research progresses, we can expect the use of polydopamine in the formulation of nanofertilizers to continue evolving, bringing significant benefits to agriculture, food security, and the environment.

Nanozeolite

Zeolite helps the crop cultivation process by improving the soil condition, increasing water utilization efficiency and enhancing the retention of nutrients. This increases the availability of nutrients in the soil and helps plants take up the nutrients for a longer period of time due to their slow decomposition rate. Moreover, it also minimizes the volatilization of ammonia and reduces soil salinity (Rai, Acharya, and Dey 2012; Reháková et al. 2004; Saadat, Reza Sepaskhah, and Azadi 2012; Sangeetha and Baskar 2016).

It is evident that nano-zeolites have a large surface area, and the coating of them can control the release of nitrogen from fertilizer. The synthesized fertilizer was demonstrated to have an extended slow release in soil without impacting the environment (Manikandan and Subramanian 2016).

It was found that ZNC exhibited considerably higher levels of water absorbency, water retention capacity, swelling ratio, and equilibrium water content than NZ, making it more favorable for use. Furthermore, the use of these nanocomposite materials is environmentally friendly and safe (Lateef et al. 2016).

Recently, zeolite-based urea has become increasingly popular for use in the development of controlled-release fertilizers (CRFs). This is due to its inherent cation exchange property, low cost, and the ability to control the nutrient release rate effectively. To fabricate CRFs with zeolite-coated urea, various binders such as potato starch, corn starch, acrylic polymer, white cement, and bentonite clay have been used. As demonstrated by Dubey and Rao Mailapalli (2019), the best results were observed when an acrylic polymer was used as a binder (UP-AP). The fabricated CRFs were then characterized using SEM, FT-IR, PSD, crushing strength, structural stability, and elemental analysis.

In this context, the use of nanozeolites in the development of nanofertilizers represents a promising direction for the agriculture of the future.

Nano-hydroxyapatite

Nowadays, many researchers have focused on nano-hydroxyapatite (nHA, $Ca_{10}(PO_4)_6(OH)_2$) based nanofertilizers as an alternative to traditional water-soluble phosphorus (P) fertilizers (Chhipa 2017; Maghsoodi et al. 2020). This mineral is the key component of human bones, teeth, and hard tissues and has been found to have the potential to improve the use of P fertilizer (Gómez-Morales et al. 2013). While commercially available P fertilizers are easily soluble in soil solution, they can be mixed with surface water bodies through runoff, resulting in eutrophication (Maghsoodi et al. 2020). nHA, however, is less soluble, thus minimizing the risk of contamination, such as eutrophication. Furthermore, it has the potential to cause slower urea or N release by forming a strong bond with urea (Kottegoda et al. 2011).

Hydroxyapatite, also known as "bone mineral" $Ca_{10}(PO_4)_6(OH)_2$), is a naturally occurring bio-compatible material with a high surface area to volume ratio found in human and animal hard tissues. Scientists have successfully loaded urea into hydroxyapatite nanoparticles (HANPs) due to its ability to deliver Ca and P. The strong bonds that form between HA and urea through its carbonyl and amine groups result in an adequate release of urea based on plants' requirements. Urea is also shielded against excessively fast release and decomposition, preventing eutrophication. Comparatively, the nutrient release test found that urea loaded HA nanohybrids released nutrients for up to a week, while urea alone released within minutes. To further evaluate the impacts of these materials, an agronomic rice (Oryza sativa L.) field trial was conducted.

Researchers have followed various methods to prepare synthetic nHA such as wet chemical precipitation (Gypser and Freese 2020), hydrolysis (Rop et al. 2019), mechanochemical (Vahdat, Ghasemi, and Yousefpour 2020), hydrothermal (Ali Ashraf et al. 2021), and sol–gel method (Maghsoodi et al. 2020).

Priyam et al. (2019) invented a novel method of biosynthesis of nHA involving phosphate releasing bacteria (Bacillus licheniformis). This method demonstrated that the biogenically produced nHA possessed similar physical and chemical properties to commercially available nHA, with no negative impact on the growth of soil bacteria.

Rop et al. (2018) formulated another SRF based on a composite of nHA and water-soluble fertilizer (urea, $(NH_4)_2HPO_4$ and K_2SO_4) in water hyacinth cellulose-graft-poly (acrylamide) polymer hydrogel for NPK. The chemical interaction between nHA, urea, and monomer was investigated by FTIR spectra and the investigation revealed HA & urea formed a complex by hydrogen (H) binding which helps to maintain a lower releasing rate of nitrogen. The authors claimed SRF that could provide a lower rate of releasing of N and P but the rate of K release was comparatively fast.

A recent study formulated a urea-hydroxyapatite nanohybrid (U-HAP) named CRUF and compared its N release aspect with other materials such as urea-impregnated biochar (UB), hydrochar (UH), and zeolite (UZ) in water and calcareous waterlogged soil (Maghsoodi et al. 2020). U-HAP was found to have the slowest release rate of N among the rest, with only 15% of it being released in more than 7 days. The Korsmeyer-Peppas model, based on the Fickian diffusion rule, was successful in describing the N release. However, the bond between urea and HAP nanorods is weak and disadvantageous, as it results in an insufficient rate of urea release for practical and large-scale use. This is due to the weak interactions between urea and HAP nanorods, such as carbonyl and amine groups, H bonds, and metal – ligand interactions between N of urea and Ca of HAP NRs, as suggested by a previous research (Kottegoda et al. 2017).

Therefore, the use of nano-hydroxyapatite in the development of nanofertilizers represents an exciting and promising prospect for the agricultural sector, with the potential to enhance productivity, sustainability, and food security in the future.

Nanoclay

Nanoclays, such as montmorillonite (MMT), hectorite, kaolin, and laponite, have been widely used in the production of nanocomposites due to their beneficial properties. These nanoclays have a nanosized thickness of bidimensional platelets and an extent of few micrometers, and are known to provide increased heat stability, swelling and solute sorption capacity, mechanical behavior, and lower production costs (Hayles et al. 2017). Additionally, they are an excellent choice for carrying nutrients such as borate, nitrate and phosphate due to their special anion exchange capacity (Benício Luíz et al. 2017; Songkhum et al. 2018). Moreover, cationic nanoclays, such as kaolinite, montmorillonite, and zeolites, are the most widely used as nutrient carriers (Lateef et al. 2016; Noh, Komarneni, and Park 2015; Roshanravan et al. 2014). Consequently, nanoclays are used not only as fertilizer carriers, but also in packaging of food and beverage, nanopesticide carrier, and medical usages (Hayles et al. 2017).

Nanoclays can be an excellent choice as nutrient carriers/coatings due to their two key features. Firstly, their structural components can provide a physical barrier to protect nutrient elements. Secondly, their layers enable intercalation of nutrients through ion-exchange or non-electrostatic interactions. These features give nanoclays immense potential to hold nutrients, increase plant growth rate, improve nutrient use efficiency, supply a balanced nutrient supply, and reduce environmental hazards (Lateef et al. 2016).

The combination of nanoclays and poly (methacrylic acid) for the synthesis of nanocomposite hydrogels yields three distinct structures, namely intercalated, exfoliated and intercalated-exfoliated. These structures form as the clay nanoparticles are dispersed in the hydrogel, with the intercalated structure indicating that the hydrogel chains are inserted between the clay platelets without disrupting their structure. The inclusion of nanoclays in the synthesis of potassium CRF increases the porous diameter of the nanostructured hydrogel coating made up of poly (methacrylic acid) and enhances its thermal stability, nutrient release duration and nutrient release amount. Furthermore, nanocomposite hydrogels containing 20% nanoclays reach equilibrium after 75 h, while hydrogels containing 0% nanoclays take just 50 h. The nanoclay also increases the interaction between the fertilizer and the matrix, limiting its release due to its lamellar structure, and resulting in a 70% higher amount of nutrients released than that of hydrogel (Junior Carlos et al. 2018).

The results of a recent study revealed that nanocomposite coatings containing nano-montmorillonite (MMT) are more effective at controlling nutrient release in water and soil than polyurethane-coated fertilizers (PU). At 25°C, the initial release rate (24 h) and nutrient release lifespan of the nanocomposite-coated fertilizer (MPU) are 4.4% and 90 days, respectively, compared to 19.2% and 26 days for PU. Furthermore, it was found that the higher the amount of nano-MMT included in the MPU, the longer its nutrient release lifespan. This is attributed to the denser polymer network structure formed by the inclusion of MMT nanoparticles into the polymer system (Jia, Zhang, and Lu 2020).

Nano-bio fertilizer

Nano-bio fertilizers have been increasingly preferred over chemical fertilizers due to their potential to offer sustainable agriculture while avoiding the adverse effects of conventional fertilizers. Nano-bio fertilizers are a combination of engineering nanoparticles and biofertilizers such as microorganisms, designed to provide sufficient nutrients to plants. These fertilizers are composed of nutrients and plant growth enriching microorganisms, which are capable of fixing atmospheric nitrogen, solubilizing phosphate, restoring soil nutrient richness, and breaking down complex organic matter into simpler compounds. Compared to chemical fertilizers, nano-bio fertilizers offer advantages such as better shelf life, greater stability, and improved performance parameters, such as pH, temperature, and radiation (Dineshkumar et al. 2018; Itelima et al. 2018).

The presence of cadmium (Cd) can cause oxidative stress in plants, leading to a decrease in chlorophyll content. However, TiO_2 nano-bio fertilizer has been found to be a nontoxic method for controlling the effects of Cd on chlorophyll content and biomass yield (Muradoglu et al. 2015).

Nanoparticles have a flexible working mechanism that allows them to enter the root and foliar entry of plants (Zulfiqar et al. 2019). Nano-assisted materials found in nanofertilizers are beneficial in mitigating various abiotic stresses such as drought (Jaberzadeh et al. 2013), salinity (Siddiqui Manzer et al. 2014), metal stress (Tripathi et al. 2015), and temperature effects (Haghighi, Abolghasemi, and da Silva 2014). As a result, nanofertilizers have become a viable alternative for soil management, reducing the need for high levels of conventional fertilizers. The proposed model of nanoparticle acquisition and translocation is depicted in Figure 4. In one possible uptake mechanism, nanoparticles can enter the intercellular space through the

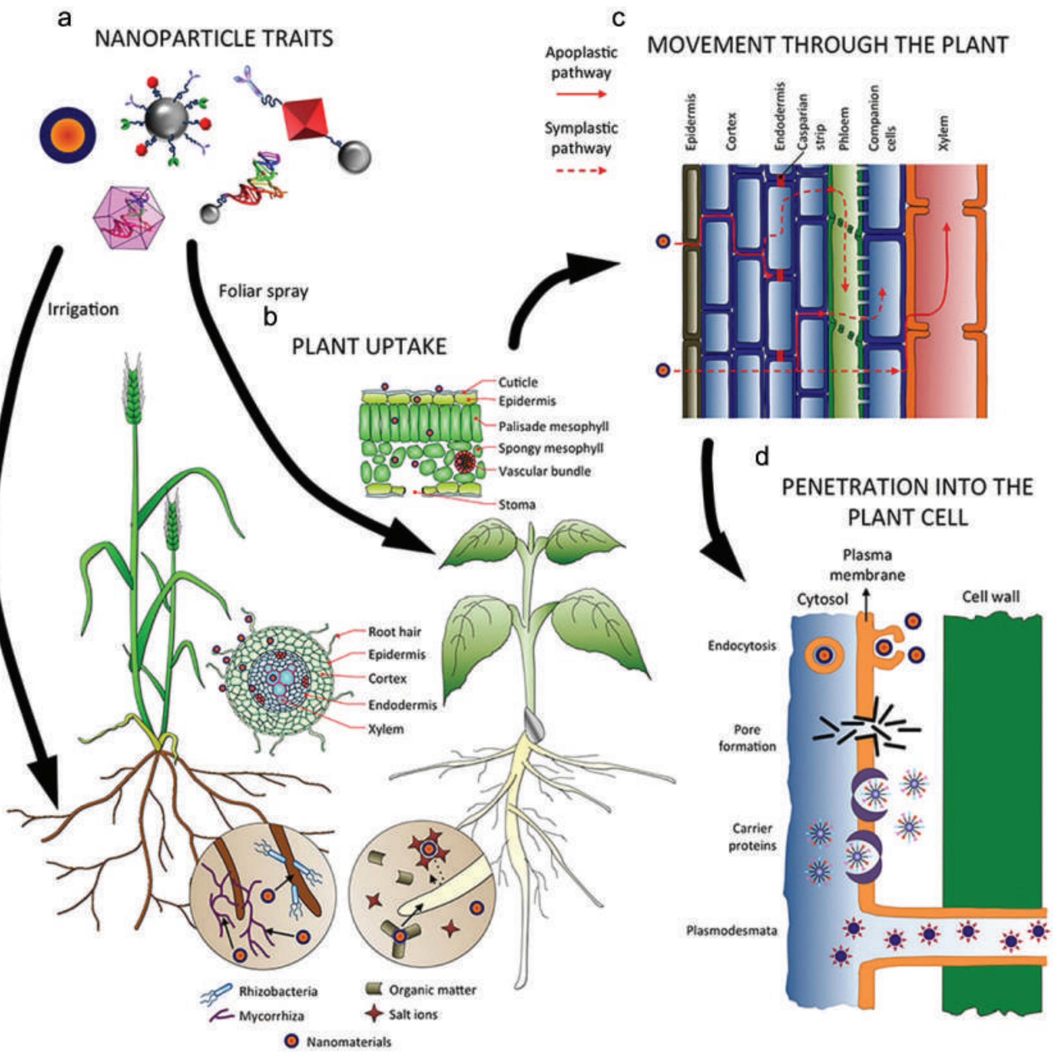

Figure 4. Schematic representation of the factors that influencing absorption, uptake, transport, and penetration of NPs in plants; (a) NPs uptake and translocated in the plant; (b) interaction of NPs with microorganisms and compounds; (c) follow the pathway of NPs for moving up and down the plant; and (d) mechanisms for the internalization of NPs inside the cell (Pérez-de-Luque 2017).

apoplastic pathway and then pass through the cell wall into epidermal and cortical cells, eventually reaching the endodermis and accumulating in uniform or aggregate form (Chhipa 2017).

As cited in past studies, slow release fertilizers are broadly categorized with respect to mechanism and type of coating material used. By viewing the past research work of Guo et al. (2005), Lin Shu et al. (2008), Trenkel (2013), the SRFs could be widely classified into three types as shown in the diagram and explained below:

(1) The first kind of organic compounds are those with low solubility. These substances can be further divided into two categories, depending on the source: natural organic materials (e.g. human and animal waste, municipal sewage sludge) and artificially man-made organic-nitrogen products. Examples of the latter, which are biodegradable and environmentally friendly, include urea formaldehyde (UF) and chemical degradable compounds such as

Isobutyledene-diurea (IBDU) and urea acetaldehyde, which derive from a condensation reaction between urea and acetaldehyde.

(2) The next important type of fertilizer is soluble in water and is typically applied to soil with irrigation. These compounds are mostly found in the form of prills or granules with a water-resistant polymer coating that degrades over time, allowing the nitrogen to be released into the soil. The polymer coating used to control the slow release of the fertilizer can be organic, such as thermoplastics or polymer resins, or inorganic, such as sulfur, gypsum, dolomite, or zeolite. The coating material used is either hydrophobic or hydrophilic, depending on the desired nutrient discharge rate to the crop in the soil.

(3) The third category includes less soluble inorganic substances containing metal-based ammonium phosphates, such as potassium ammonium phosphate (KNH_4PO_4 and $MgNH_4PO_4$) and acidified phosphate rock ($H_2PO_4^-$).

Slow release fertilizers can be divided into two categories according to the mechanism by which they gradually release nutrients: "failure mechanism" and "diffusion mechanism."

The nutrient release behavior and rate are the most important properties for coated fertilizer, so most authors have generally tested the release rate using water (Elhassani et al. 2019; Lu et al. 2019, 2020; Sarmah and Karak 2020; Saruchi, Mittal, and Alhassan 2019), soil (Chen et al. 2020; De et al. 2020), or both systems (El Assimi et al. 2020; Xu et al. 2020), while a small number of researchers have used saline solutions (Meftah et al. 2021). To ensure accurate comparisons, distilled water is typically used as the environment for release testing, as it eliminates the large differences encountered in regard to soil properties and climate conditions.

The release behavior of nitrogen through coated fertilizer in water and soil is not the same. Vudjung and Saengsuwan (2018) found that 100% of the nitrogen was released within 24 days in soil, compared to only 3 days in water. This finding was corroborated by El Assimi et al. (2020) and Baki and Abedi-Koupai (2018), who reported that around 60% of nitrogen was released in soil after 30 days, while in water, around 35% was released within 10 days. However, Jia et al. (2013), documented the opposite effect, with a faster release rate of nitrogen in soil than in water. This discrepancy demonstrates the complexity and heterogeneity of the release of NPK in different environments, making it difficult to determine the exact release mechanisms.

The release of nutrients from polymer-coated fertilizers has been a topic of debate among researchers. While it is challenging to pinpoint a single mechanism to explain the controlled-release of nutrients, this occurs through diffusion through a semi-impermeable membrane

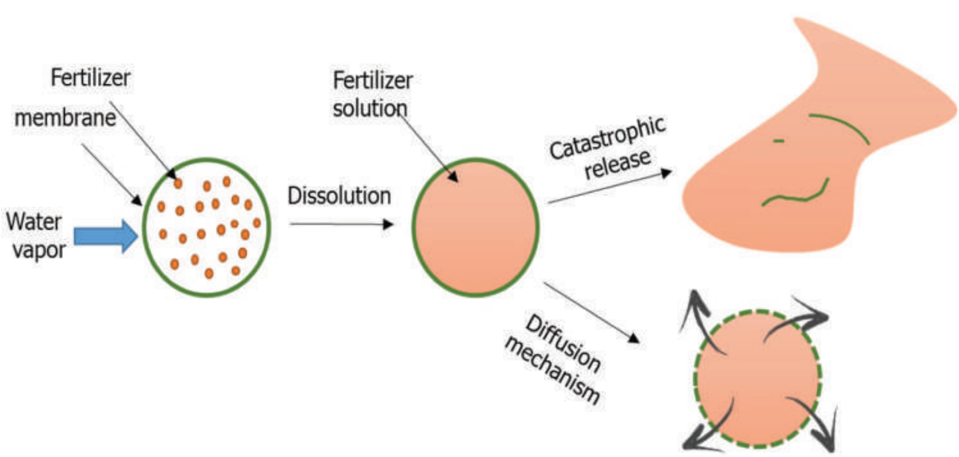

Figure 5. Release mechanisms of nutrients through a polymeric coating when in contact with water (or soil solution).

(Figure 5). In the diffusion mechanism, the content is released slowly by diffusion, determined by the concentration or pressure gradient across the coating. In the failure mechanism, or catastrophic release, the entire content is released due to the rupture of the coating, followed by the bursting of the granule. This is typically seen with non-elastic coatings such as sulfur-based coatings. In contrast, biopolymer-coated fertilizers are known for their slow-release mechanism (Fertahi et al. 2020).

The release of nutrients from polymeric coated fertilizers, particularly double-coated fertilizers with a superabsorbent outer coating. In the first stage, the outer layer swells and transforms into a hydrogel, allowing for a dynamic exchange between the free water in the hydrogel and the water in the soil. Once the free water has migrated to the middle layer, water slowly penetrates through the inner coating and compounds in the fertilizer dissolve. Here, diffusion is the rate-limiting step in the release. In the last stage, the middle layer degrades, releasing the nutrients into the outer layer where they diffuse out and enter the soil. The degradation rate in this stage determines the nutrient release rate. These interactions between the fertilizer granule and the polymer layer are physical rather than chemical (Lubkowski et al. 2015).

A significant body of literature has developed on the toxicological interactions of ENMs with plants, with a focus on hazard assessment through short-term, high-dose exposures often under model conditions. However, there has been relatively less research on the potential beneficial effects of ENMs on plants (Dimkpa Christian and Prem 2018).

The release rate of nutrients from polymer-based coatings is greatly affected by a variety of parameters, such as the nature of the polymer (hydrophilic or hydrophobic), their concentration in the coating solution, the solution viscosity, added modifying agents, the number of layers, and the techniques used for the coating. These parameters interact to determine the thickness and porosity of the coating layer, ultimately influencing the rate of nutrient release (Costa Milene et al. 2013; Jarosiewicz and Tomaszewska 2003; Pérez-García et al. 2007; Riyajan, Sasithornsonti, and Phinyocheep 2012; Tomaszewska, Jarosiewicz, and Karakulski 2002).

The coating methods used to create a nutrient-release layer on fertilizer granules have an effect on the quality of the coating, which is an important factor to consider when controlling the nutrient release rate. Immersion is a common method for coating granules, however, it can cause partial dissolution of water-soluble fertilizers, and may cause granules to stick together if the solution is viscous. For this reason, the rotating pan method is a better alternative, as it minimizes mechanical damage to the beads and reduces attrition. However, this method is not as effective at creating a uniform coating layer, which can lead to uneven nutrient release (Naz and Anwar Sulaiman 2016; Sahni and Chaudhuri 2012; Sedighikamal et al. 2015). On the other hand, the fluidized bed method is more effective at creating uniform coating layers, but the aggressive granule movement can cause mechanical stress and attrition, which can also affect the quality of the coatings (Agrawal Anjali and Pandey 2015; Werner Stephen et al. 2007; Wu and Liu 2008).

The quality of coat-forming can be greatly affected by the compatibility between components. When the components are not mutually compatible, two or more phases can form in the same coating, resulting in an uneven film that can have cracks and pinholes. To improve the mechanical and adhesion properties of polymeric membranes, plasticizers, crosslinkers, or compatibilizers are often added to coating formulations (Fertahi et al. 2019; Lü et al. 2014; Pérez-García et al. 2007). With these properties in place, the shell can withstand the internal pressure created by contact with water, allowing for a slow and steady release of nutrients without breaking down. Niu and Li (2012) observed that the presence of plasticizers will slow down the release of ammonium nitrate, likely due to the formation of a film without cracks, thereby decreasing the permeability of water and the rate of nutrient diffusion. Furthermore, blending, grafting, and copolymerization of various biopolymers or biopolymers with synthetic components can be used to create effective coatings. Riyajan, Sasithornsonti, and Phinyocheep (2012) demonstrated the effectiveness of coating urea with natural rubber reinforced by grafting with modified cassava starch (NR-g-ST) – the capsule N release was only 21% within 24 hours, a significant decrease from the 100% release within 8 hours that was observed with starch-only coating. This decrease in diffusion rate could be attributed to the chemical interaction between natural rubber and starch due to the grafting interaction.

The release rate of nutrients decreases as the polymer concentration in the coating solution is increased, due to a greater thickness and lower porosity in the coating layers of fertilizer granules. This was observed by Niu and Li (2012), who found that coating formulations with 10% ethyl cellulose in the coating solution produced layers on coated urea that were less thick (49 μm) compared to 70 μm with 20%.

Fertilizer granules can be coated with a single (Beig et al. 2020), double (Cui et al. 2020; El Assimi et al. 2020; Qiao et al. 2016), or triple layer (Noppakundilograt, Pheatcharat, and Kiatkamjornwong 2015) using various coating solutions and techniques. The most common is a single layer, which is made using one of the previously mentioned techniques. For double and triple layers, the second layer is usually a superabsorbent to provide extra protection and release of nutrients. Multiple layers with the same solution are usually obtained using the immersion technique, whereas different solutions are used for double layers. This type of fertilizer is particularly useful in arid climates, as the multiple layers increase the coating thickness and decrease its porosity, creating a more compact structure and lower porosity than a single coating.

Biochar is seen as an optimal material to use for CRFs due to its cost-effectiveness, renewability, environmentally-friendly properties, recyclability, and attractive physico-chemical properties. However, agronomists and economists do not support the use of high amounts of biochar (>10 t ha^{-1}) due to the lack of essential macronutrients N, P, and K that it provides. As a result, biochar-based fertilizers are created by combining fertilizers, particularly P fertilizers, with biochar through direct mixing, copyrolysis, compounding, co-composting, absorbing nutrients from a solution, and microwave production (B. Liang et al. 2010). Raw materials used for producing biochar, such as plant wastages, organic wastes, wood chips, and animal manure are inexpensive, abundant, renewable, and biodegradable sources of materials (Baiamonte et al. 2015; Tammeorg et al. 2014; Varma Rajender 2019).

It is possible to improve the performance of coating fertilizers by using activated carbon as a substitute for conventional biochar. To determine if biochars can be used to make high-performance activated carbon, their physicochemical and morphological features should be assessed (Hassan et al. 2021). Activated carbon is a mesoporous carbon material that is characterized by its large specific surface area, adjustable pore structure, fair pore size distribution, functional groups within the carbon network, strong surface reactivity and relative cost-effectiveness (Yahya Mohd Adib and Ngah 2015). Therefore, exploring the potential of activated carbon in formulating controlled-release fertilizers is essential in order to ensure sustainable agricultural practices (Rahman et al. 2021).

As seen, certain nanofertilizers can potentially improve crop yield and nutritional content compared to conventional methods. However, more research is needed to fully understand the mechanisms involved, in order to optimize these benefits and minimize any negative outcomes. Different crops and soil types have unique nutritional or fertilization requirements, so the development of smart, responsive and tunable materials is essential.

When assessing the effects of engineered nanomaterials (ENMs) on plants as nano-fertilizers or nano-pesticides, it is important to compare their effects against those of the corresponding conventional equivalents. Studies have claimed positive outcomes, yet this should be done in order to ensure accuracy and accuracy of results (Dimkpa Christian and Prem 2018; Kumar et al. 2019; Sathiyabama and Manikandan 2018).

Although the use of nanofertilizers promises potential new approaches toward smart and sustainable agriculture, the potential risks associated with their application should also be carefully considered before their commercialization. The bioaccumulation and long-term exposure of nanomaterials in the environment and food chain may pose a threat to human health (Bundschuh et al. 2018; Tiede et al. 2016). Moreover, the application of nanofertilizers raises several safety and ethical issues that need to be addressed before commercial use.

Therefore, further research is necessary to investigate the long-term effects of nanofertilizers on the environment, plants, soil organisms, and human health before their commercial application.

Very recently Rajput et al. (2020), discussed the toxicity of CuO and ZnO nanoparticles (NPs) on soil organisms and human health, which could help to regulate their application in the agriculture sector. It was elucidated that these NPs can pass through various chemical and biochemical reactions, potentially damaging plant cells and posing a serious threat to human health.

In order to ensure proper nutrient supply to plant growth and improve fertilizer use efficiency, novel biodegradable and renewable coating materials with superhydrophobicity need to be designed and developed. These materials should be modified and manufactured in an ecological and cost effective way, and have the capability to regulate the release of nutrients in accordance with the growth timeline or nutrient requirement of crops. This would reduce the imbalances caused by the inadequate hydrophobicity of natural-materials-based coating materials, allowing for more effective and efficient fertilizer use.

Conclusion

The escalating challenges faced by the global agricultural system due to the increasing population, biotic and abiotic stresses, environmental contamination, and climate change demand urgent and innovative solutions. Traditional agricultural practices relying heavily on chemical fertilizers and pesticides have led to harmful consequences for human health, ecosystems, and sustainability. As the demand for food rises, the indiscriminate use of fertilizers has also increased, resulting in environmental pollution. Nanofertilizers, a product of nanotechnology-based delivery systems, offer a promising alternative.

In this context, key topics were discussed, such as macro and micronutrients, controlled and slow release of nutrients, and wall materials, demonstrating the growing importance of nanofertilizer technology for modern agriculture, in which the use of unconventional sources of nutrients applied to nanofertilizers has shown significant promise.

The controlled and slow release of nutrients, a fundamental aspect of nanofertilizers, contributes to the minimization of nutrient wastage, reducing leaching and environmental impact. This also promotes a more efficient use of nutrients, conserving resources and enhancing crop yields.

Wall materials play a crucial role in the effectiveness of nanofertilizers. Polymers, zeolites, polydopamine, and other advanced materials enable the encapsulation of nutrients and controlled release, ensuring that nutrients are delivered according to the plants' needs.

In this way, advances in nanofertilizer technology and their innovative carriers offer a promising approach for modern agriculture. This technology is revolutionizing how nutrients are delivered to plants, promoting sustainability, reducing environmental impact, and improving agricultural productivity. As research and development in this field continue, we can expect nanofertilizers to play an increasingly important role in the agriculture of the future.

As research and development in nanofertilizer technologies continue to advance, several exciting prospects emerge. It is possible to envision the integration of nanotechnology with the capability to provide specific nutrients to each plant, enabling highly targeted and effective fertilization. This promises to enhance resource efficiency, such as reducing water usage and minimizing excess nutrients, thus contributing to more cost-effective and environmentally friendly agriculture.

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Data availability statement

The data that supports the findings of this study are available from the corresponding author.

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