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The Perspectives on the Application of Biopolymers for a Sustainable Agriculture

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ABSTRACT

One of the main challenges for modern agriculture is to seek methods for improvement of crop growth and quality which is based on the sustainable agriculture to provide the growing population with access to high-quality food. Controlled-release fertilizers (CRF) and slow-release fertilizers (SRF) are the answer to these challenges, as they constitute an alternative means of achieving higher agronomic efficiency relative to traditional fertilizers. The focus of this paper is to review the changes and trends regarding the CRF/SRF, with a particular focus on biopolymer-coated fertilizers, specifically sodium alginate as both the biopolymer for coating and a soil conditioner. The presented literature review reveals the promising prospects related to the necessity of developing fertilizers with a controlled/slow release of minerals, involving materials that provide the appropriate mineral release rate and which are characterized by properties ensuring a substantial reduction in the negative impact on the natural environment. This finds confirmation in the clear tendency for applying biodegradable materials, particularly originating from natural sources, which may become the appropriate materials used for fertilizer coating when considering the new requirements concerning environmental issues.

Keywords: agriculture, biopolymer, sodium alginate, slow-release fertilizer, controlled-release fertilizer.

INTRODUCTION

The growth of the global population, which is projected to reach 8.5 billion in 2030 and 9.7 billion people in 2050 (World Population Prospects 2022: Summary of Results), leads to an increase in the demand for food. Therefore one of the main challenges for modern agriculture is to seek methods for improvement of crop growth and quality by implementing sustainable agriculture to provide the growing population with access to high-quality food. The answer to this challenge is found in novel methods and technologies applied in the agrochemical industry, including slow-release fertilizers (SRF) and controlled-release fertilizers (CRF). Sustainable agriculture also constitutes a significant issue from the perspective of the progressing climate change, both in the context of water management and the availability of water resources [Li et al., 2022], as well as concerning environmental pollution and progressing biodiversity loss [Kumar et al. 2023]. Furthermore, climate change leads to an imbalance in the food supply, which makes it difficult to face the challenges related to meeting the constantly rising demand for food resulting from the growing population number, particularly in developing countries [Wang et al., 2023]. The White Paper (COM(2009)147) (White Paper – Adapting to climate change: towards a European framework for action (COM(2009)147)) is a significant strategic document of the European Commission that defines the European framework for facing the consequences of climate change. It made it possible to include this adaptation in key EU political fields – the health and social policies, agriculture and forestry, biodiversity and ecosystems, water management and water resources, coastal regions and marine areas and economic sectors. Furthermore, "A farm to fork strategy" constitutes a key element of the European Green Deal (The European Green Deal COM(2019) 640), factoring in the challenges pertaining to the need to implement sustainable food systems in a comprehensive manner, as these provide benefits on multiple levels, including in terms of environmental, social, health and economic advantages (A Farm to Fork Strategy for a fair, healthy and environmentally-friendly food system COM(2020) 381).

A surplus of nutrients (particularly nitrogen and phosphorus) in the environment, resulting from excess agricultural exploitation, as well as situations where not all nutrients used in agriculture are effectively uptake by the plants, constitutes a significant source of air, soil and water pollution, while also exerting an influence on the climate (A Farm to Fork Strategy for a fair, healthy and environmentally-friendly food system COM(2020) 381). It is estimated that the use of conventional fertilizers results in the uptake of only about 50% of nitrogen [Govindasamy et al., 2023], less than 25% of phosphorus [Chowdhury and Zhang, 2021] and 10–50% of potassium [Madzokere et al., 2021]. Due to the high solubility and low thermal stability of conventional fertilizers, the majority of nutrients released from these fertilizers migrate to the environment, which results in low plant fertilization efficiency [Lubkowski, 2016]. Intense fertilization may also lead to significant environmental problems through the increase in greenhouse gas concentrations [Martínez-Dalmau et al., 2021] and heavy metal contamination [Mitra et al., 2022], as well as water quality deterioration [Dębska et al., 2021]. Nitrogen-based fertilizers have also been reported to be the source of N_2O, which is the primary substance responsible for depletion of the stratospheric ozone layer [Pan et al., 2022]. Furthermore, the use of traditional fertilizers may result in excess soil compaction, which is also determined by factors such as the type and humidity of soil, resulting in the emergence or acceleration of other soil degradation processes, such as erosion or landslides, as well as contributing to the decreasing water retention capability of arable land. The rate of nutrient release is acknowledged as the primary disadvantage of conventional fertilizers, as it is different from the rate of nutrient uptake by the plants [Mikula et al., 2020]. Another significant factor that influences environmental pollution is the mineral fertilizer production process itself, considering that it emits e.g. sulfur oxides, nitrogen oxides, fluorine compounds and particulates. The low bioavailability of minerals is also unfavorable from the economic perspective: the nitrogen loss, energy and human labor lower the economic balance of the entire process [Matson et al., 1998; de Vries, 2021]. Continuous research for more sustainable production includes developing fertilizers based on raw materials, with a reduced consumption of energy within their production processes. Examples include the use of alternative raw materials such as sewage sludge ash and poultry litter [Gorazda et al. 2023], as well as extensive research on coated fertilizers [Benlamlih et al., 2021: Moradi et al., 2024].

COATED FERTILIZERS

Fertilizers such as CRF and SRF are the answer to the challenges and problems described above, as they constitute an alternative means of achieving higher agronomic efficiency relative to traditional fertilizers due to their slow and/or controlled release of nutrients, which is intended to achieve better synchronization with the plant growth cycles, thereby minimizing environmental pollution. For example, slow-release or controlled-release nitrogen fertilizers offer an alternative for achieving higher agronomic yields compared to traditional fertilizers. The efficiency of the polymer-coated controlled-release fertilizer (CRF) was compared with other slow-release fertilizers and traditional fertilizers in microscale experiments as well as in a large field experiment by Gil-Ortiz et al. (2020). In the microscale experiment, CRF-fertilized plants had 35% higher yields compared to plants treated with conventional fertilizer as well as about 24% increase in N levels in the leaves of CRF-treated plants (Gil-Ortiz et al. 2020). SRF/CRF can increase fertilizer efficiency by 10–30% compared with instant nitrogen. Moreover, it is possible to obtain the same yield at a dose of 10-40% lower compared to conventional fertilizer, and in some cases, only one application of CRF is required, which can reduce labor costs by 75% [Singh, 2023]. Additionally, the use of CRF fertilizers contributes to the reduction of osmotic stress or burning of roots and leaves caused by high concentrations of soluble salts, which may occur when conventional fertilizers are used. The potential benefits of CRF include improving soil quality and germination rates while reducing stem breakage and disease infestation. CRFs can also increase nutrient availability and accumulation of protein material in plants, leading to higher yield [Fertahi et al., 2021]. Mustafa et al. (2022) reviewed the literature in the area of sulfur and zinc-coated urea in soil, their impact on crop production, nitrogen use efficiency (NUE), the residual and toxic effects of coated urea, and the constraints of adopting coated fertilizers [Mustafa et al., 2022]. For example, Sanderson and Fillmore (2012) have evaluated and compared various SRFs (sulfur-coated urea, methylene urea, commercial UFLEXX) with ammonium nitrate used in soil for 3 years. All tested SRFs enhanced the carrot yield compared to conventional fertilizers [Sanders and Fillmore, 2012].

Novel fertilizers provide plants with nutrients at the desired rate and concentration, thereby prolonging their activity in the soil. By improving the plant nutrient use efficiency, these products simultaneously constitute a more economic and environmentally friendly fertilization system. Novel fertilizers of this type provide plants with nutrients at the desired rate and concentration, thereby prolonging their activity in the soil. By improving the plant nutrient use efficiency, these products simultaneously constitute a more economic and environmentally friendly fertilization system [Kalia et al., 2020; Mikula et al., 2020; Lawrencia et al., 2021]. However, the major challenge for agriculture is not only to control nutrient losses but also to control water losses [Salimi et al., 2023].

According to a general definition, a fertilizer is considered to be a CRF or SRF if it contains plant nutrients in a form conducive to the delay of their bioavailability to plants for purposes of absorption and use, or which extends the nutrient bioavailability to plants compared to a reference conventional fertilizer [Salimi et al., 2023]. According to a more detailed definition, SRFs are "low solubility compounds with a complex/high molecular weight and a chemical structure that release nutrients through either microbial or chemically decomposable compounds", whereas CRFs are defined as "products containing sources of water-soluble nutrients, the release of which in the soil is controlled by a coating applied to the fertilizer" [Lawrencia et al., 2021; Kontárová et al., 2022]. According to the international standard ISO 18644 (2016) (ISO 18644:2016 fertilizers and soil conditioners, controlled-release fertilizer, general requirements), controlled-release fertilizers (CRF) are defined as fertilizers that extend the bioavailability of nutrients to be absorbed and used by plants after application or which delay their bioavailability to plants for much longer relative to conventional fertilizers. The European Committee for Standardization has defined three criteria for CRF: (1) >15% of the nutrients must not be released within the first 24 hours after applying the fertilizer; (2) >75% of the nutrients must not be released within the first 28 days after applying the fertilizer; (3) at least 75% of the nutrients must be released over the provided release time. These criteria ensure that the nutrients are released from the fertilizer in a controlled and gradual manner over a given time, contributing to optimal plant growth while minimizing nutrient loss and/or leaching [Naz and Sulaiman, 2017; Fu et al., 2018].

Despite the numerous advantages of CRF/SRF, the potential limitations of their application should be indicated as well. The first is the economic factor, specifically their price, which is considerably higher compared to conventional fertilizers. Another limitation concerns the accumulation of substances used to produce the polymer coating in the soil. Synthetic materials used for coating may be poorly degradable, leading to soil contamination. For example, the accumulation of microcapsules derived from coated fertilizers in rice fields was studied in Japan. In all of the rice fields tested, contamination was detected at concentrations in the range of 6–369 mg/kg (average 144 mg/kg) - much higher than the concentrations of microplastics in agricultural fields in other countries [Katsumi et al., 2021]. According to Executive Summary Fertilizer Outlook 2019–2023 [Executive Summary Fertilizer Outlook 2019–2023, IFA International Fertilizer Association] the EU is also working on biodegradability criteria for polymer coatings of controlled-release fertilizers. In response to this challenge, current research in the area of coated fertilizers is focusing on developing CRFs using environmentally friendly and safer coating materials that can provide better performance in controlling release rates, but also not cause secondary environmental pollution. Although it is possible to adapt and modify synthetic polymers to obtain the desired CRF properties, polymers that do not undergo biodegradation may exert a negative impact on the environment. Furthermore, for example, the application of CRF such as sulfur-coated urea (SCU) in large quantities may increase the soil acidity [Lawrencia et al., 2021]. The advantages and disadvantages of CRF are compiled in the Figure 1 below.

The terms CRF and SRF are typically used to define next-generation fertilizers, which are often referred to as "smart" fertilizers. Sometimes the terms CRF and SRF are used interchangeably [Fertahi et al., 2021]. For the nutrients to be released from SRF, they must first be decomposed through microbial activity. SRF are acknowledged to include fertilizers from plant and animal sources, compost, as well as, for example, urea-formaldehyde fertilizer, isobutylidenediurea and crotonylidene diurea. The release of nitrogen from SRF occurs primarily with the participation of soil microorganisms, therefore it is strongly dependent on the soil's microbiological activity, which means that the release rate cannot be controlled. Furthermore, the microorganism efficiency depends on other factors such as the type, humidity and temperature of soil [Fu et al., 2018; El-Aziz et al., 2021]. On the other hand, CRF are distinguished from SRF by both the production technology and the manner of nutrient release. CRF are coated fertilizers, where the nutrient release is controlled by a physical barrier. Fertilizer granules can either be coated in one or more layers using the same coating solution or in two or three layers using different solutions and using the same or different coating techniques. Single and double layers are the most common [Fertahi et al., 2021].

The focus of this paper is to review the changes and trends regarding CRF, with a particular focus on biopolymer-coated CRF, specifically including sodium alginate. Numerous attempts at developing effective and appropriate methods for preparing highly-efficient CRF, inspired by drug delivery systems, are undertaken to face the challenges and environmental problems related to the use of conventional fertilizers and to prevent irrational fertilizer management in agriculture [Ganetri et al., 2020].

THE MECHANISM OF NUTRIENT RELEASE FROM CRF

Nitrogen (N), phosphorus (P) and potassium (K) are the primary macronutrients that find common application in global agriculture. CRF are generally classified as single-component fertilizers such as polymer-coated urea (PCU) or compound fertilizers that contain three primary nutrients: nitrogen, phosphorus and potassium (NPK). There are also numerous preparations that contain calcium, magnesium, sulfur and micronutrients. The duration of phytoavailability refers to the strongly soluble fraction of an element that is absorbed by a plant [Ganetri et al., 2020]. The fertilizer coating constitutes a selectively permeable or semi-permeable membrane. When CRF is applied to an appropriately humid arable substrate, the granule coating facilitates a unidirectional passage of water towards the granule by osmosis, which leads to the swelling of the granule under the influence of the absorbed water. The nutrients inside the coated granule are partially dissolved. The water entering the granule becomes a high-concentration solution, which increases the hydrostatic pressure in the coated fertilizer. Afterwards, the nutrients are slowly released by diffusion under the influence of the concentration and/or pressure gradient, and the nutrient availability in the soil affects the mechanism of nutrient release from the fertilizer. Fertilizers coated

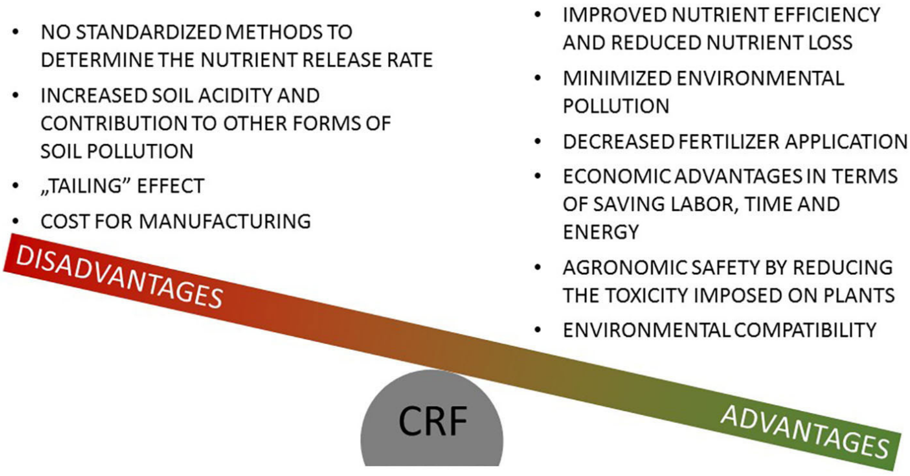

Figure 1. Advantages and disadvantages of CRF [own elaboration based on Lawrencia et al., 2021]

in macromolecules undergo a release process known as the diffusion mechanism. The nutrient diffusion rate from the granules to the soil depends on the solubility and availability of the nutrient in the soil itself. In practice, the difference in concentration between the two media (soil and CRF core) controls the nutrient release rate. When nutrients that occur naturally in the soil are not available (are poorly soluble), the nutrient release rate from the CRF to the soil increases. The availability of N from organic or mineral sources varies greatly. Plants uptake N in the form of nitrite or ammonium ions through the roots from the soil solution. However, the root system of most cultivated plants explores only 20–25% of the available soil volume over one year due to the competition for the available nutrients between the soil and the plant roots in the soil-plant system [Lustosa Filho et al., 2019]. Therefore a significant part of the applied N fertilizer is lost over the year by one of three types of processes/reactions – microbiological, chemical and physical, which lower its availability to plants [Ganetri et al., 2020]. Apart from the slow nitrogen release, these fertilizers also exhibit a water retention capability, which simultaneously increases the efficiency of both the fertilizer and water resource use. Furthermore, the rate of nutrient release from CRF is often dependent on temperature, as its increase leads to an expansion of micropores, enabling the diffusion of a greater quantity of nutrients. The nutrient release is determined by the coating thickness as well [Azeem et al., 2014; Ganetri et al., 2020]. Additionally, the coated fertilizer release rate depends on the density, crystallinity and solubility of the external membrane materials [Kwan and Davidov-Pardo, 2018]. In the case of hydrogel materials, the nutrient release mechanism is different compared to conventional coating systems. It was observed that in systems of urea delivery based on a hydrogel matrix, the nutrient release profiles in the intermediate stationary phase were linear and as zero-order release kinetics, whereas their constant release rates were not controlled by the gel strength. This phenomenon could be attributed to the combined effects of Fick's diffusion and erosion release [Caccavo et al., 2016].

Because sodium alginate has hydrogel properties and the ability to retain water, the nutrient release profile from alginate fertilizer differs from the release profile from capsules coated with other polymers. In the case of polyurethane-coated urea (PCU), it could be observed that the cumulative N release rate from PCU increased steadily until day 21, reaching a value of 5% of cumulative N release. From day 21, a faster nitrogen release could be observed, up to a value of approximately 15% measured on day 35. For capsules coated with inorganic materials such as sulfur-coated urea (SCU), N is released rapidly and linearly until day 7. Then, the cumulative release rate of SCU gradually stabilized. On day 35, approximately 40% of the nitrogen is released [Tong et al., 2018]. The nitrogen release profile from alginate-coated capsules is similar to that of inorganic-coated capsules. Mesias et al. (2019) observed that nitrogen and other nutrients (potassium, phosphate) are released quickly and linearly until the 20th day, after which the process is slower and stabilizes. About 40% of NPK was released over a period of 30 days and this is consistent with the norm, which is less than 70% for 28 days [Mesias et al., 2019].

COATING TECHNIQUES

Fertilizer coating can be performed by various mechanisms, such as coating with semi-permeable or impermeable materials, protein materials or other chemically degradable forms, by the slow hydrolysis of water-soluble compounds of low molecular mass or by occlusion. The coating material controls the water penetration and nutrient availability in forms preferred by plants while facilitating crop maximization [Chandran et al., 2020]. Generally, CRF coating methods can be divided into physical and chemical. The main physical methods include: spray coating by means of a rotary drum or a disc granulator, fluidized bed technology, melting and molding. On the other hand, the typically named chemical methods are: polymerization in a solution, inverse suspension polymerization and microwave radiation [Lawrencia et al., 2021]. Advantages and disadvantages of fertilizer coating techniques are summarized in Table 1.

COATING MATERIALS

The coating materials are divided into two main categories: inorganic materials and organic polymer materials. Inorganic materials used for coating include: hydroxyapatite [Maghsoodi et al., 2020], zeolite [Dubey and Mailapalli, 2019; Maghsoodi et al., 2020], gypsum and phosphogypsum

Table 1. Fertilizer coating techniques – advantages and disadvantages

Techniques	Innovations, examples of the fertilizer products	Advantages	Disadvantages	References
Rotary drum	Soil-mimetic eco-friendly fertilizer	Easily scaled, low-cost, continuous proces, ease of adapting the technique to the coated material	The thickness of the coating layer depends of the materials used, requires a lot of materials to achieve a coating	[Sahu et al., 2024]
Melting & extrusion	Smart fertilizer prepared via extrusion	Simple, low-cost, and solvent-free	The equipment is expensive, hot melting is involved	[Bi et al., 2020]
Pan coating	Ethylcellulose-coated materials	Low operating costs, easy scaled, continuous process	The manufacturing process is sensitive to changes in humidity and high air temperature during drying	[Lubkowski et al., 2019]
Fluidized bed	Poly(tannic acid)-Coated Urea Fertilizer Hydrophobic octadecylamine-polyphenola	Low operating cost, easily scaled. wide selection of materials, uniform coating, careful formula development and precise process control	Expensive equipment, long residence time, possibility of solvent explosion and filter clogging	[Wang et al., 2020; Sun et al., 2020]
Inverse suspension polymerization	Superabsorbent, slow release nitrogen fertilizer	Efficiency, easy to obtain spherical, uniform particles of a specific size and shape, possible solvent recovery, possibility of adding various functional groups and additives to the polymer structure, waste minimization, environmentally friendly	The process parameters such as speed, mixing time, temperature and reaction pressure must be carefully selected and optimized	[Liu et al., 2007]
Solution polymerization/cross-linking	Degradable slow-release fertilizer based on ionic crosslinked hydrogel material	Clear, homogenous coatings with high mechanical andadhesive qualities	A large amount of solvent is needed, high process costs, negative impact on the environment, low nutrient release efficiency due to strong diffusion resistance	[Xu and Guo, 2023]
Microwave irradiation	Slow release fertilizers based on starch-based hydrogels	Low energy consumption, low process costs and environmental effects, fertilizer coating process controllable and regulated.	Requires specialized tools and precautions, due to the heat generated during the coating process, thermal degradation of the coating is possible, which in turn leads to an uneven coating or insufficient adhesion of the coating material to fertilizers.	[Chen et al., 2023]

[Vashishtha, 2010], sulfur [Mehmood et al., 2019] and attapulgite [Ni et al., 2011]. The organic polymer materials are further divided into synthetic (polyurethane, polyethylene, polystyrene, alkyd resins, polyacrylamide, polyacetal, polydopamine, polyolefins, polyvinyl alcohol) [Lawrencia et al., 2021] as well as naturally biodegradable polymer materials, such as alginate and chitosan [Majeed et al.,2015; Mesias et al., 2019], lignin [Majeed et al., 2015], cellulose [Pang et al., 2019], starch [Mehmood et al., 2019; Salimi et al., 2023], natural rubber [Vudjung and Saengsuwan, 2018], carrageen [Akalin and Pulat, 2020], bio-based polyurethane [Lu et al., 2022]. Other organic materials that however are not polymers include biochar [Ding et al., 2017; Shi et al., 2020] and rosin adduct [Mumtaz et al., 2019]. Their application may also promote the chemical and biological properties of soil as well as ion exchange. Producing combined coatings for fertilizers, prepared based on different biopolymers (blending, copolymerization) or biopolymers and synthetic materials, was subjected to studies as well [Fertahi et al., 2021]. The tested materials included: natural rubber and starch [Roziafanto et al., 2020], starch and poly(acrylamide-co-acrylic acid) [Salimi et al., 2020] as well as sodium carboxymethylcellulose and hydroxyethylcellulose [Ronga et al., 2020].

NATURAL POLYMER-BASED COATINGS

The method of coating fertilizers with biodegradable polymers constitutes an efficient way of controlling the nutrient release rate from the fertilizer to the soil [Ganetri et al., 2020]. Coating makes it possible to obtain a high nutrient content in the total fertilizer granule mass by covering it with a thin layer of the coating on the surface [Calabi-Floody et al., 2020]. This is unlike the case of matrix-based fertilizers, where the nutrient content in the total fertilizer mass is much lower than in coated fertilizers, as they need to be mixed with the other materials. Therefore this paper focuses on coated CRF due to their high potential for providing crops with nutrients in the face of environmental challenges. Significant progress has been noted over the last decades in the development of modern biopolymer-based coatings for CRF, due to both the great number of materials appropriate for such applications as well as the versatility of their properties and their biodegradability [Calabi-Floody et al., 2020]. Analyses in mathematical modelling and simulation techniques are also being carried out to characterize and mechanism the release of nutrients from CRF [Irfan et al., 2018]. Although it is possible to modify synthetic polymers to obtain the desired properties, such polymers may generate a significant impact on the environment since they do not undergo biodegradation. After the nutrients are released from the granules, the coating residues in the form of polymer materials may accumulate in the soil to a volume of 50 kg/ha per year, resulting in considerable soil pollution [Lubkowski et al., 2015]. Because of this situation, researchers are increasingly more interested in the possibility of applying natural polymers that are biodegradable, non-toxic and acknowledged as environmentally friendly.

Information concerning the origins of a biopolymer – which is significant in the context of its availability, extraction and purification method as well as a number of other key physicochemical properties – is required to select the appropriate biopolymer useful in CRF production. Some studies reveal that the release rate for fertilizers coated in lignin, cellulose and starch is too high [Yang et al., 2012]. Cellulose and starch are hydrophilic polymers due to the presence of hydroxyl groups (-OH) on their surface, whereas starch exhibits poor mechanical properties. Lignin consists of heterogeneous biopolymers, is water-soluble and incompatible with hydrophilic polymers such as chitin and cellulose, which are highly crystalline [Azeem et al., 2014; Majeed et al., 2015]. To overcome the aforementioned limitations, biopolymers are also subjected to various chemical and physical modifications. For example, chitin can be modified by deacetylation and converted into chitosan [Santos et al., 2020], which is characterized by solubility and coating generation properties. Coating solutions are also complemented with crosslinking agents, compatibilizers and plasticizers that influence the elasticity, tensile strength and adhesion of the polymer coatings [Fertahi et al., 2021]. The most commonly employed natural polymers for CRF coating include: starch, cellulose, lignin, alginate and chitosan as well as bio-based polyurethane (PU), bio-based modified alkyd resin, polysulfone (SO_2 and eugenol-based), latex and natural rubber [Lawrencia et al., 2021]. The Table 2 below presents a compilation of example latest data concerning CRF coated in natural polymers.

Latest literature reports contain numerous references to the development of effective coated CRF production methods using natural polymers. However, natural polymers are commonly applied in combination with other materials for composite formation, as the natural polymers alone do not exhibit the appropriate mechanical integrity and other properties ideal for fertilizer coating as required to produce CRF [Lawrencia et al., 2021]. As part of the studies performed by Mesias et al. (2019), a coated nitrogen-phosphorus-potassium (NPK) fertilizer was prepared by chitosan and alginate crosslinking using citric acid. Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), particle size analysis and zeta potential measurement revealed correct crosslinking as well as adequate size and colloidal stability. Studies of release behavior under various pH demonstrated that the Chi/Alg NPK conforms with a controlled-release fertilizer standard with a maximum release of 40% over 30 days. Testing the release mechanism via the Korsmeyer-Peppas model revealed that the nutrient release was controlled by both the coating material relaxation as well as the diffusion process [Mesias et al., 2019]. Ma et al. (2023) developed a multifunctional double-layered fertilizer (DCRF), where urea was used as the core, while the inner coating was formed from bio-based polyurethane and the hydrogel outer coating was produced from sodium alginate and copper ions. Furthermore, the alginate was modified using mesoporous silica nanoparticles with sodium selenate. Applying the DCRF improved the yield and nutritive value of cherry radish (*Raphanus sativus*

Table 2. Natural polymer-based CRFs

Type of fertilizer	Coated material	Modifier	Release duration	Additional properties	References
NPK	Chitosan (low molecular weight) Sodium alginate (low molecular weight)	–	Approximately 40% of NPK was released for the period of 30 days	–	[Mesias et al., 2019]
Urea	Bio-based polyurethane, Sodium alginate and copper ions	Mesoporous silica nanoparticles loaded with sodium selenate	N and Se release longevity of DCRF reached 42 days and 40 h, respectively	Antifungal, significantly improved yield, selenium concentration and procyanidin content of cherry radish	[Ma et al., 2023]
Phosphorus fertilizer	Polyolefin wax, polyurethane prepared from castor oil	–	Initial release rate of 0.22% and release longevity of 93.4 days	Increased particle hardness, decrease in the porosity and the reduction of special surfaces inside the particles	[Lu et al., 2019]
Ammonium nitrate	Alginate	Biogenic silica	15% of the nitrogen was released within 24 h and 56% over 28 days. The complete nitrogen dissolution was achieved after 60 days	–	[de Matos et al., 2018]
Urea	Low molecular weight chitosan	Salicylaldehyde	Urea released in three stages: (i) a burst effect in the first 5 h - up to 46% urea passed in the water medium, (ii) next 11 days - a slower release reaching 75% urea, (iii) a slower continuous release in the next 23 days when almost all the urea passed in the water medium	Good water absorbency and hydrolytic stability	[Iftime et al., 2019]

L. var. radculus pers) due to the elevated contents of selenium as an essential trace element. Additionally, the DCRF exhibited an antifungal effect on *Fusarium oxysporum* Schltdl. The developed multifunctional fertilizer exhibits great potential in terms of means for the sustainable development of agriculture [Ma et al., 2023].

Thus far, few works have been focused on coating phosphorus fertilizers, particularly diammonium phosphate (DAP), due to its irregular shape and large specific surface. Lu et al. (2019) applied an innovative technology focused on modifying the granule surface, developed based on wax and biopolymer coating (CDAP). For this purpose, DAP was modified using polyolefin wax and coated in polyurethane prepared based on castor oil. The experiment results revealed that the wax modification considerably decreased the specific surface and improved the hardness of the fertilizer while also considerably facilitating the formation of the biopolymer-based coating. Furthermore, the CDAP prepared based on the wax-modified DAP exhibited a more efficient controlled release compared to a CDAP prepared based on regular DAP. The obtained results demonstrate that wax modification constitutes an effective technology for producing high-efficiency controlled-release phosphorus fertilizers [Lu et al., 2019]. Knijnenburg et al. (2021) developed beads containing nanoparticles of zinc oxide (nano-ZnO-containing beads) entrapped in biodegradable polymer beads consisting of alginate and polyvinyl alcohol. In that way, prepared beads exhibited a slow release of Zn, whereas the PVA addition led to an increase in the water absorption and retention. This nano-Zn beads are promising for Zn fertilizer applications under the conditions of limited water availability [Knijnenburg et al., 2021].

BIOPOLYMER AS A SOIL CONDITIONER BASED ON THE EXAMPLE OF SODIUM ALGINATE

Soil provides not just structural support for root growth, but primarily supplies plants with nutrients, water and air, forms a habitat for soil microbiota, and also constitutes an enormous carbon reservoir, which is significant in the context of the progressing climate change. Therefore, maintaining the appropriate soil quality becomes a necessity for sustainable agriculture, food safety and the environment [Lal 2015, Kopittke et al., 2019; Tahat et al. 2020). It was demonstrated that applying soil conditioners enhances the physical and structural properties of soil as a result of improved cohesion and porosity, and may also prevent soil erosion, optimize the soil structure, increase water retention and improve nutrient supply efficiency. Particular attention was devoted to alginate as a promising biopolymer for broadly agricultural applications [Tomadoni et al., 2020; Du Toit van der Merwe et al., 2022]. Apart from applying alginate as a coating material in CRF, its use may also contribute to improving soil fertility by increasing the nutrient availability in the soil. Excessive fertilizer application in the prior decades has led to an accumulation of phosphorus in the soil [Tian et al., 2022]. However, its bioavailability was greatly limited due to its propensity for sedimentation with calcium, iron, aluminum and other elements under various conditions of soil humidity and pH. Alginate may contribute to increasing the phosphorus availability in the soil [Ge et al., 2022]. Furthermore, alginate, a polysaccharide known for its biodegradable, non-toxic and hydrogel properties, has found broad application as a substance for improving the water retention capacity of the soil due to its water absorption capability [Song et al., 2020].

A significant rise in interest in microbiological fertilizers has been noted in recent times. The potential use of alginate as a polymer matrix for microorganisms is being explored in the field of agro-industry [Martínez-Cano et al., 2022]. However, the application of beneficial soil microorganisms is often burdened with numerous difficulties due to adverse environmental factors and competition with native microorganisms. Research focused on alginate as the carrier for microorganism encapsulation is being conducted to face these challenges and develop microbiological fertilizers. The obtained test results indicate that alginate-based hydrogels are effective carriers in microbiological fertilizers [Shin et al., 2023].

Soil structure degradation is constantly accelerated by adverse environmental conditions, climate change and negative anthropogenic activity. Biopolymers, particularly alginate, exhibit promising qualities for soil structure improvement. The interactions of alginate with soil particles facilitate particle aggregation in soil, leading to an improvement in its stability as well as beneficial structural changes [Soltani et al., 2021]. Furthermore, biopolymer-based hydrogels are capable of soil particle rearrangement through their matrices, improving the soil particle cohesion, strengthening soil aggregates and modifying water retention and fluid dynamics, thereby enhancing the mechanical stability of the soil environment [Buchmann et al., 2020]. Alginates are also used in soil mulching, consequently promoting plant growth. For example, a sodium alginate solution mixed with algae micromolecules (*Undaria pinnatifida*), acting as a biostimulant, when sprayed on the topsoil resulted in increased fresh/dry matter, increased chlorophyll content and decreased anthocyanin levels (stress index) in cultivated tomato plants [Merino et al. 2021].

All in all, alginates are a subject of interest to many scientists conducting research aimed at preserving healthy soils for sustainable agriculture. Despite the potential benefits resulting from the broad opportunities for alginate application in agriculture, there are still a few barriers to its commercial use. One of it is the variability of alginate properties. The physical, mechanical and biological properties of the alginate polymer and its derivatives exhibit fluctuations depending on factors such as seasonal differences and geographical origins. This variability may hinder the preparation of standardized products fit for large-scale production [Peteiro, 2018; Hurtado et al., 2022]. One should also take into account the potential degradation or aging processes of biopolymers in the soil [Buchmann et al., 2020].

CHALLENGES AND PERSPECTIVES FOR FURTHER RESEARCH ON CRF/SRF

The use of slow-release or controlled-release fertilizers can reduce the problems associated with the use of conventional fertilizers. However, there are still a number of challenges involved in using "smart" fertilizers. The greatest challenge related to the use of SRF/CRF is the "tailing effect", which decreases the economic benefits resulting from the use of SRF [Shaviv, 2001]. The accumulation of the material used to form the polymer coatings in the soil is another significant problem. Fertilizers coated in synthetic materials may be poorly degradable, which can lead to soil contamination. Although it is possible to adapt and modify synthetic polymers to obtain the desired CRF properties, the use of polymers that do not undergo biodegradation may exert a considerable negative impact on the environment. Furthermore, the high cost of coating materials constitutes another barrier for the common application of CRF in agriculture [Lawrencia et al., 2021].

A further challenge is found in standardizing the methods for determining nutrient release rates from CRF in a reliable manner, as there is insufficient correlation between data obtained from laboratory testing and the actual nutrient release rates in practical applications that may be available to consumers. The CRF release rate is strongly dependent on the methodology selected for its assessment. Generally, four methods can be identified: (1) immersion in water, (2) leaching through the soil, (3) greenhouse observation and (4) yield comparison. Immersion in water is the simplest method of assessing the nutrient release rate from a fertilizer, though its results are far removed from the actual state. The key issue is to determine the relationship between the results obtained by means of various assessment methods and the actual release rate. Greenhouse observation and yield comparison appear to be the most appropriate methods. They find broad application, particularly for final assessment and control, but their weaknesses related to the time necessary for the assessment and the unpredictable weather conditions constitute significant limitations to their use. The various methodologies for CRF release rate assessments should be modified depending on the tested products. The methodologies should also be adapted to the laboratory capabilities. It is obvious that different plants require different soil conditions for proper growth. Therefore fertilizers should also be assessed under different soil conditions, and the assessment method should be adequate for the growth conditions of a given plant [Duan et al., 2023].

CONCLUSIONS

To conclude, a promising prospect is offered by the research aimed at developing fertilizers with a controlled/slow release of minerals, involving materials that provide the appropriate mineral release rate and which are characterized by properties ensuring a substantial reduction in the negative impact on the natural environment. In light of the above considerations, a clear tendency can be identified as regards applying biodegradable materials, particularly originating from natural sources, which may become the appropriate and eco-friendly materials used for fertilizer coating, given the new requirements concerning environmental issues.

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