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Recent Trends in Organic Coating based on Biopolymers and Biomass for Controlled and Slow Release Fertilizers

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Abstract

The growth of the human population is causing an exponential increase in the need for food. Fertilizers are one of the most important elements to meet this increased demand and to ensure global food security. Many enhanced efficiency fertilizers, such as controlled-release fertilizers (CRFs) have been developed. Although these fertilizers offer many advantages over prior generations, their high cost of production as well as unfavorable effects on the environment and soil quality have limited their use. To mitigate these issues, CRFs based on biopolymers (CRF@BB) represent a new generation of fertilizers produced by coating the granules with biopolymers. In addition to controlling the nutrient release rate, these products also enhance the soil quality and they reduce the negative effects associated with conventional fertilizers. This review summarizes the recent advances in biopolymers and derived biopolymers used in the area of CRF@BB, the coating technologies, and the parameters governing the release behavior through organic coating materials, as well as the effect of coated CRFs on the soil and plants growth.

Keywords: Fertilizer, soil, plant, biopolymer

Content

1. Introduction

In light of the continuous growth of the earth's population, the number of humans is expected to increase from 7 billion in 2014 to approximately 9.5 billion by 2050 [1]. Moreover, global food needs have increased in parallel with the continued exponential growth of the earth's population. According to the United Nations Food and Agriculture Organization (FAO), food production needs to increase by 70% to supply the projected 2050 population [2]. On the other hand, there is less and less arable land due to urbanization, industrialization, desertification, etc. To respond to the increasing food requirement, farmers are applying enormous quantities of fertilizers to maximize the agricultural yield. The world consumption of nitrogen (N), phosphate (P_2O_5), and potash (K_2O) fertilizers in 2015 was reported to be 110,027,000; 41,151,000; and 32,838,000 tons, respectively, and forecasts for 2020 are estimated to be 118,136,000; 45,853,000; and 37,042,000 tons, respectively [3]. However, this strategy suffers from a number of limitations and generates other harmful problems, due to agricultural practices and technic as well as the quantities sometimes used in excess. Plants only consume part of nutrients and the rest is lost in the environment due to rain, irrigation, fixation, volatilization, etc. This causes environmental, economic, and health problems, in addition to negative effects on the physiology and the growth of plants, as well as nutrition quality [1,4–8]. Recently, a number of alternative fertilizers were developed based on biochar [9], using thermochemical processes (pyrolysis, hydrothermal carbonization, etc.) with digestate [10] and compost [11] obtained after anaerobic and aerobic digestion of biomass, respectively, and a combination of biochar-digestate. These biofertilizer formulations enrich the soil, enhance its properties, and make nutrients available for the plant. Biofertilizers based on microorganisms have also been developed in recent years [12–15]. In general, these microorganisms are thought to solubilize the otherwise insoluble nutrients, particularly from mineral rocks, and to maintain the continuum of nutrient flux available to plant roots. However, mineral fertilizers remain the richest and most effective source of nutrients. Controlled- and slow-release fertilizers (CRFs/SRFs) are specifically designed fertilizer that releases active fertilizing nutrients in a controlled delayed manner matched with the sequential needs of plants for nutrients. Thus, they provide enhanced nutrient use efficiency and enhanced yields without suffering from nutrient loss [1]. Coating of mineral fertilizers is one way to produce CRFs/SRFs. Over time, researchers have adopted a variety of coatings. Sulfur was tried initially as a coating agent [16,17]. It was an attractive candidate for coating, but its low wettability and adhesion to the coated core, and the need for conditioning materials to reinforce its sealing, add additional expense to the final product. Moreover, any sulfur remaining in the soil can react with water, thereby acidifying the soil. Subsequent research efforts have focused on polymeric materials. These materials are not disturbed as readily by microorganisms like sulfur coatings [1]. However, another problem arose, namely the majority of polymers need an organic solvent, such as dichloromethane [18], N, N-dimethyl-formamide (DMF) [19], or chloroform [20], which are harmful to the environment. Additionally, most of these polymers are not readily biodegradable after total nutrient release; which then creates a new source of soil pollution as they lead to an undesirable accumulation of plastic residues up to 50 kg/ha/year [21]. To overcome these economic and environmental obstacles, the research focus is shifting towards biopolymers. The choice of biopolymers did not occur by chance; these materials are cheaper than conventional coating materials [22,23]; they are biodegradable, biocompatible, and nontoxic; and they contribute to improvement of the soil quality [24,25].

The aim of the present review is to provide an overview of biopolymers from biomass and biodegradable synthesized polymers, focusing mainly on their promising properties as an organic coating of mineral fertilizer for agricultural applications. Firstly, we briefly have described the characteristics and properties of different biopolymers used for mineral fertilizer coating. Secondly, we have explored the literature regarding their use as new and smart biobased coating organic materials for controlled release mineral fertilizers. Thirdly, we have detailed their advantages and disadvantages and their impact on soil and plant. Fourthly, we have given an overview of the different coating methods. Finally, we have proposed and discussed some perspectives and challenges for objective to improve the use of biopolymers as an organic coating for agronomic applications.

2. Background regarding controlled-release fertilizers and slow-release fertilizers (CRFs vs. SRFs)

2.1. Definition, legislation, and classification of CRFs vs. SRFs

Release and slow-release have been defined by Trenkel [26] as follows:

- Release: The transformation of a chemical substance into a plant-available form.
- Slow-release: The release rate of a nutrient from the fertilizer must be slower than that from a fertilizer in which the nutrient is readily available for plant uptake.

According to Trenkel [26], a fertilizer can be described as slow-release if the nutrient or nutrients declared as slow-release meet, under defined conditions – including at a temperature of 25 °C, three criteria in soil:

- 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.

SRFs are fertilizers in a form that release, or convert to a plant-available form, plant nutrients at a slower rate relative to an appropriate reference soluble product. Regarding CRFs, they are engineered to provide nutrients over time at a predictable rate under specific conditions.

SRFs/CRFs can be broadly classified into three major categories [1,27–30]:

- **Organic substances**: These are divided into organic-N, low-solubility, and natural compounds. The former can be divided into biological decomposing compounds that are usually based on urea-aldehyde condensation products, such as urea-formaldehyde (UF), and chemically decomposing compounds, such as isobutyledene-diurea (IBDU) or urea acetaldehyde/cyclo diurea (CDU). The latter includes crop residues, manure, slurry, composts, sewage sludge, organic-mineral fertilizers (e.g., meat and bone meal, hoof and horn meal, rapeseed meal, treated leather meal, etc.).
- **Inorganic low-solubility compounds**: Fertilizers such as metal ammonium phosphates (e.g., $MgNH_4PO_4$), and partially acidulated phosphate rocks (PAPR).
- **Water-soluble fertilizers with physical barriers:** These barriers can be generated either by coating cores or granules with sulfur/polymer materials, or by incorporating nutrients into matrices that restrict dissolution of the fertilizer. Coated fertilizers can be further divided into fertilizers coated with organic polymers that are either thermoplastic or a resin, fertilizers coated with inorganic materials such as sulfur-or mineral-based coatings, and fertilizers coated with a mixture of sulfur and organic polymers. The matrices can be produced by hydrophobic materials such as polyolefins, rubber, etc., and gel-forming polymers (hydrogels). In the past, sulfur was used for coating, but it is rarely used nowadays. Matrices based on hydrophobic materials or gel-forming polymers are used, but they are less common compared to coated CRFs. The most used category comprises granule/core fertilizers coated with organic polymer materials.

2.2. History and scientometric analysis of SRFs/CRFs

The first use of the term SRFs dates back to the 1920s, but the concept of SRFs was not recognized and was not described until the 1960s by Oertli and Lunt, Woerther, White and Hansen [31–35]. Nevertheless, most of the advances occurred in the 1980s and 1990s. Fig. 1 shows the most well-known applications of slow/controlled-release fertilizers developed over the past 60 years. In 1955, the first commercial SRFs product was developed in the USA, and it was based on urea and formaldehyde (UF) condensation compounds. This was greatly improved by combining it with polymers (urea-formaldehyde-polymer URP) in the early 1960s. Sulfur-coated urea (SCU) is one of the most common types of coated fertilizers, and it is a slow-release fertilizer made by coating urea with sulfur and wax. SCU was developed in the USA during the 1960s. However, due to the relatively poor performance of SCU, a polymer-coated SCU (PSCU) was introduced to the market. This hybrid coating offered better release of nutrient elements, and it was developed in 1969. NPK fertilizers coated with sulfur were developed for the first time in Japan in 1975, while polymer-coated NPK was first produced commercially in California starting in 1967 under the brand name “Osmocote”. The resin used as the coating material is based on a copolymer of dicyclopentadiene and glycerol ester. The first controlled nutrient-releasing fertilizer in the world was manufactured in late 1976 by Chisso-Asahi Fertilizer Company. This involved encapsulation of NPK fertilizers inside a coat based on polyolefin, and the product is called “Nutricote”. In the same context, the company SAG (Germany) developed polyurethane-coated NPK in 1982, under the trade name “Plantacote”. Polyon [36] is a similar product that was developed in 1988 by Pursell Industries, and it is based on the application of an ultra-thin polyurethane membrane coating. The first application of biopolymers organic coating fertilizers was developed by Otey et al. [37] and was based on starch as a coating material to produce controlled-release of urea (starch-urea). The coating fertilizers with chitosan and alginate was not reported until 1990, by Teixeira et al. [38]. In 1996, Garcia et al. [39] developed lignin-based controlled-release coatings for urea fertilizers.

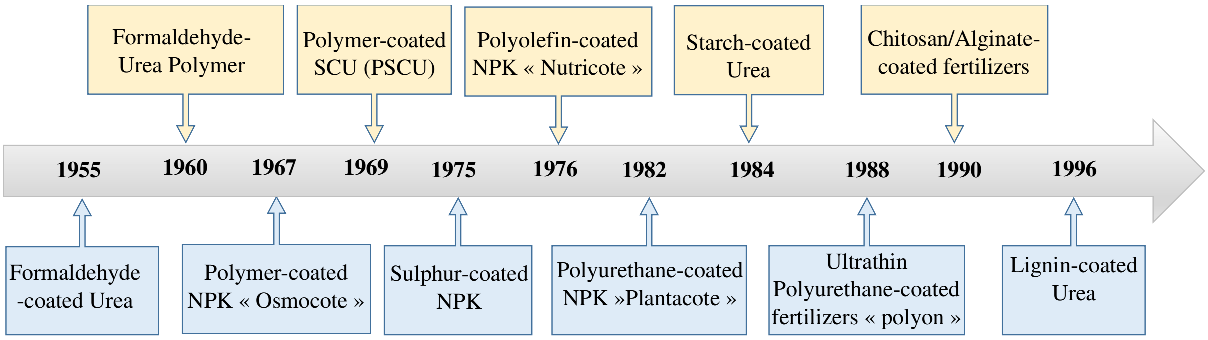


Fig.1. Chorological development of CRFs/SFRs

According to the IHS Markit Chemical Economics Handbook [40]: Controlled- and slow-release fertilizers Report, the global demand for SRFs/CRFs reached more than 1.5 million metric tons in 2018, and it is expected to grow by nearly 6% in 2022. In terms of consumption volume, China is the primary world market for slow- and controlled-release fertilizers, with a consumption rate of 46%, followed by the United States, Western Europe, and Japan [40] (Fig.2).

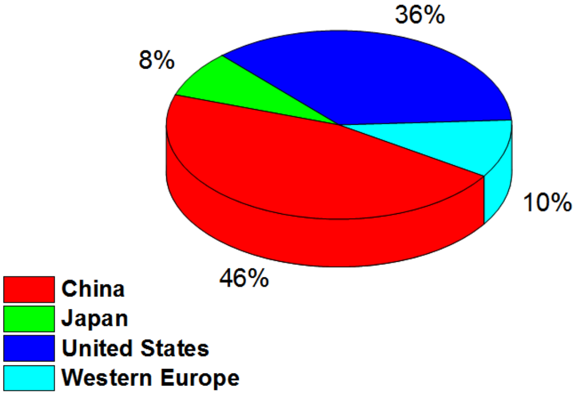
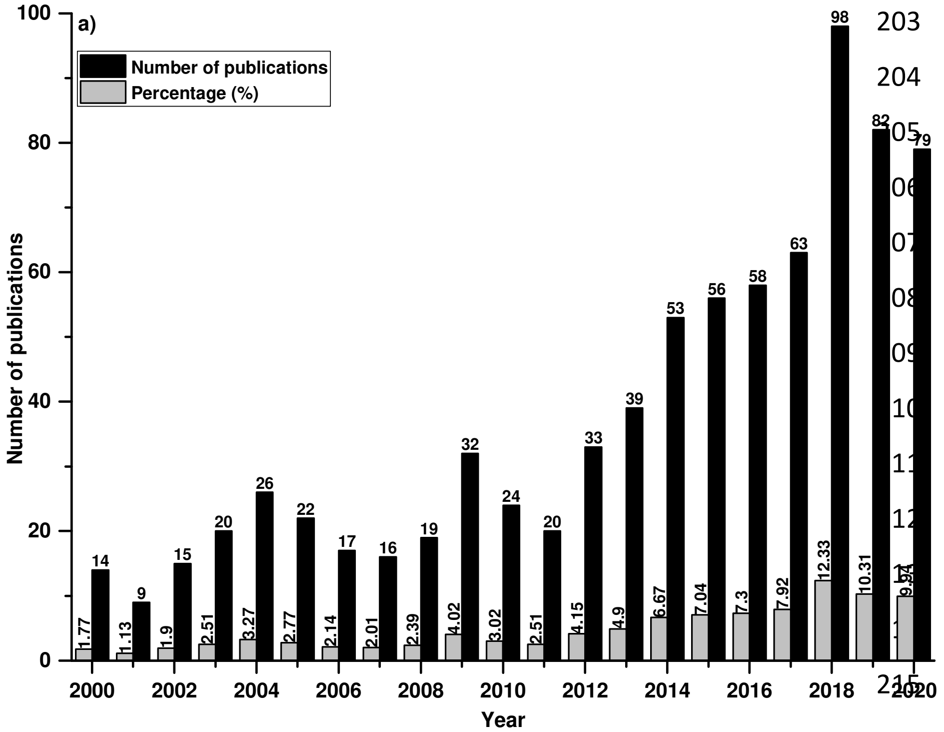


Fig. 2. Total consumption of Slow/Controlled Release Fertilizers in 2018 [40]

According to the Web of Science database, since 2000, 795 indexed research articles have been published using the keywords‶ Polymer coated fertilizers″ ,‶ Controlled release fertilizers″and ‶Slow release fertilizers″ in title. According to the collected data (Fig. 3a) and the evaluation of keywords in terms of frequency, the keyword "Controlled release fertilizers" with its occurrence frequency of 389 ranked first, accounting for 48.2% of all global publications in this field, followed by "Slow release fertilizers" with 379 (47.7%) and then the keyword "Polymer coated fertilizers" with 33 (4.1%). Also based on this data, the publications related to the field showed significant growth from 14 in 2000 to 98 in 2018, and the number of publications continues to increase exponentially (Fig. 2b). This is a clear indication of the increase in the number of studies investigating this topic.


a)
Number of publications
Percentage (%)
Number of publications
Year
0
20
40
60
80
100
2000
2002
2004
2006
2008
2010
2012
2014
2016
2018
2020
14
9
15
20
26
22
17
16
19
32
24
20
33
39
53
56
58
63
98
82
79
1.77
1.13
1.9
2.51
3.27
2.77
2.14
2.01
2.39
4.02
3.02
2.51
4.15
4.9
6.67
7.04
7.3
7.92
12.33
10.31
9.94

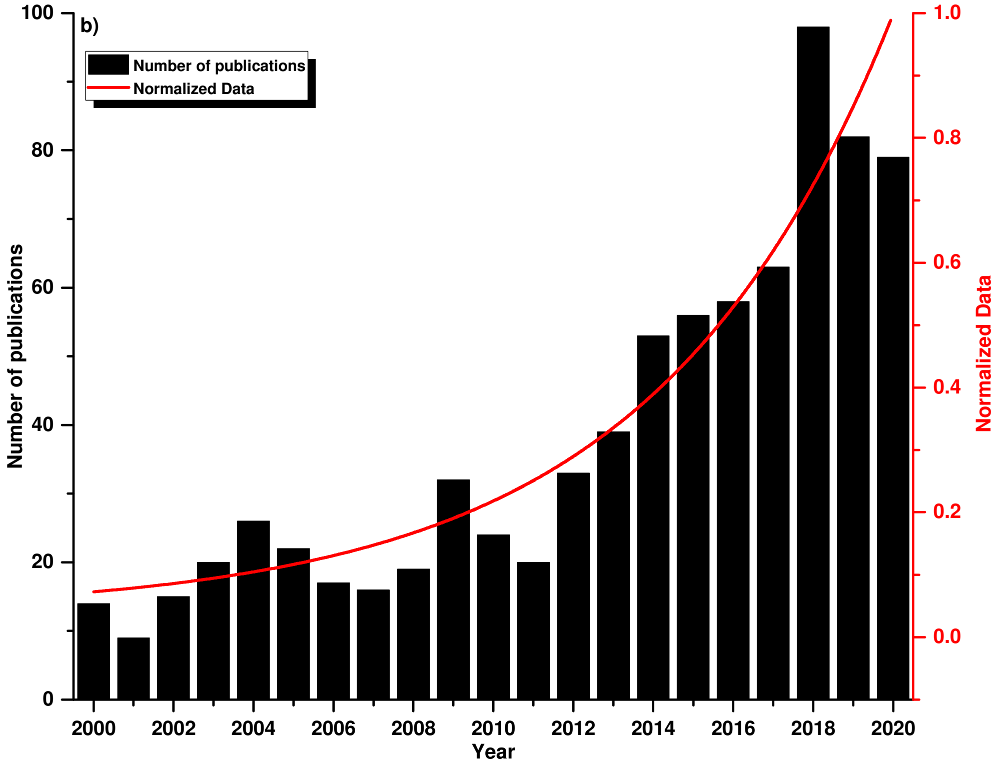

b)
Number of publications
Normalized Data
Number of publications
Normalized Data
Year
0
20
40
60
80
100
0.0
0.2
0.4
0.6
0.8
1.0
2000
2002
2004
2006
2008
2010
2012
2014
2016
2018
2020

Fig.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.

2.3.Advantages and disadvantages of SRFs/CRFs

"Controlled Release Fertilizers (CRF)" and "Slow Release Fertilizers (SRF)" are both used to describe this new generation of fertilizer, but the two terms have different meanings. We believe that we cannot really control the release of a fertilizer, and that rather depends on the coating properties (i.e. composition, porosity, and thickness; solubility of the coating materials and the core materials, etc.); and soil properties (soil type, soil pH, temperature, moisture, microbial activities, etc.). However, to differentiate these two categories of CRFs are generally related to fertilizers coated or encapsulated with inorganic or organic matter. Polymer coated fertilizer is an example of CRFs. Concerning SRFs, they include plant manures, animal manures and compost that need to be broken down by microbial activity before the nutrients can be released. They also include UF, IBDU, and CDU [41]. In addition, CRFs allow a much more controlled rate and duration of nutrient release with semi-permeable coatings. While for SRFs, the duration of release in a slow release fertilizer cannot be controlled due to the effectiveness of microbial organisms. In this review we will use the term CRFs because we will focus on the coated fertilizers".

CRFs overcome numerous problems associated with conventional fertilizers in addition to presenting several advantages economically, environmentally, and physiologically. Nevertheless, CFRs also suffer from a number of disadvantages, and research should be intensified to address these problems. We will provide a detailed account of the main problems related to conventional fertilizers and the solutions provided by CRFs as well as the associated inconveniences.

- ***Environmental and health impact:*** Plants only consume part of conventional fertilizers and the rest is lost in the environment [42]. Approximately 40–70% of the nitrogen content is lost through leaching, mineralization, NH_3 volatilization, gas emissions (nitrous oxide NOx), soil erosion, and denitrification processes. In terms of phosphorous, 80–90% is lost due to surface run-off and mineralization (fixation of P and formation of Fe- and Al-based oxides), and 50–70% of the potassium is lost mainly by leaching associated with water movement in the soil and surface run-off [43]. In addition to the economic loss, this high level of nutrient loss also gives rise to environmental issues. Nitrates from nitrogen fertilizer sources can contaminate groundwater by leaching and accumulation from agricultural activities, which can cause serious and immediate effects on human health because of the consequent deterioration of the quality of drinking water. N volatilization also pollutes the air and gives rise to adverse atmospheric effects and hazardous emissions, with consequent dermal irritation and inhalation problems. Phosphorus overflow gives rise to the eutrophication phenomenon in freshwater and estuaries; which overstimulates the growth of algal blooms and contributes to a wide range of water-related problems including summer fish kills, foul odors, and unpalatable tastes in drinking water. Excessive fertilizer use can negatively affect soil quality through acidification, persistent organic pollutants, and heavy metal accumulation [6]. CRFs have the potential to reduce the nutrient losses, as well as to minimize the potential negative effects and the risk of environmental pollution described previously and associated with overdosage [44]. Despite their positive effects, CRFs can also result in a number of negative effects that merits to be addressed. The main problem with CRFs is the use of slowly or non-degradable materials. Some types of polymers used in the coating are degraded extremely slowly or not at all in soil. Their use may lead to an undesirable accumulation of plastic residues, up to 50 kg/ha/yr, and 500 kg/ha takes almost ten years to be decomposed to just 200 ppm of dry soil [1,7,26,29,44]

- ***Agronomic effect:*** CRFs have agronomic advantages related to the improvement of plant growth conditions. These enhanced-efficiency fertilizers slowly release the nutrients to match with the plant nutrient demands and to ensure synchronization with crop requirements. Additionally, plants derive an advantage from the fertilizer due to the absence of osmotic stress or the burning of roots and leaves caused by the high concentration of soluble salts with conventional fertilizers. Further possible benefits are that CRFs improve the soil quality and germination rates while also reducing stalk breakage and disease infestation. CRFs can increase nutrient availability and the accumulation of proteinaceous material in plants, thereby resulting in higher yields [26].
- ***Economic impacts:*** By reducing nutrients loss, CRFs can generate savings in terms of the quantity of the fertilizer. A decrease of 20 to 30% of the recommended application rate of a conventional fertilizer is possible when CRFs are used, while still

maintaining the same yield [26]. Savings can also be achieved in terms of the labor, time, and energy involved. Indeed, 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 [26]. 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.

3. CRFs based on biopolymers (CRF@BB) and biodegradable polymer coatings

In this review, we focus on the coating of mineral fertilizers based on biopolymers and biodegradable polymers, referred to as "biofertilizers based on biopolymers (CRF@BB) and biodegradable polymers coatings".

3.1. Biopolymers and biodegradable polymers used as organic coatings for CRFs

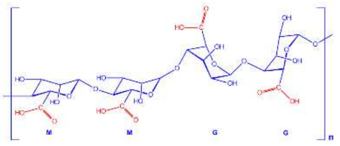
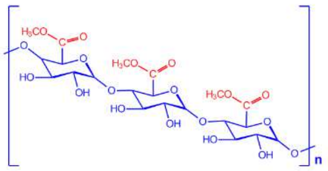
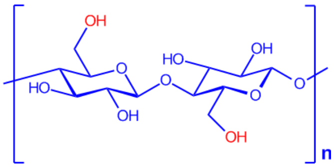
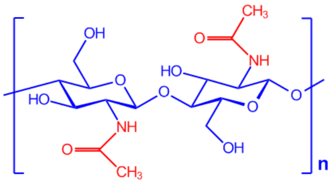
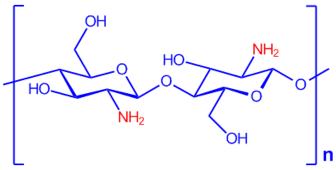
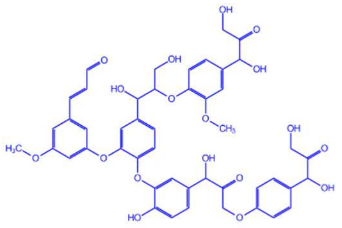
There is a lack of consensus regarding the definition of a biopolymer; some researchers define it as a polymer derived from biomass, produced by living beings (plants, algae, animals, fungi, etc.). Others say that every biodegradable, biocompatible, and nontoxic polymer can be considered to be a biopolymer, even if it is generated by synthetic means, e.g., polylactic acid, PLA [45]; polyvinyl alcohol, PVA [46,47] polybutylene succinate, PBS [48]; and polydopamine [49]. Throughout this review, we use the term 'biopolymers' to mean polymers derived from naturally available and renewable resources, i.e., starch [50], lignin [51,52], cellulose derivatives [53–55] chitosan [56–59], carrageenan [60], guar gum [61], xanthan gum [62], natural rubber [63], etc.

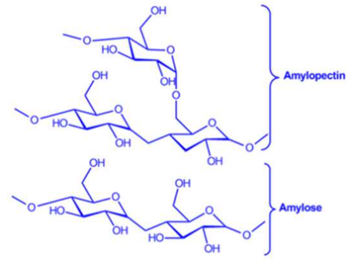
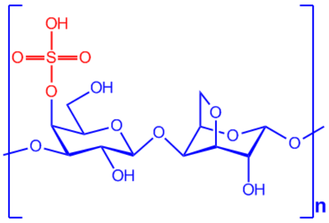
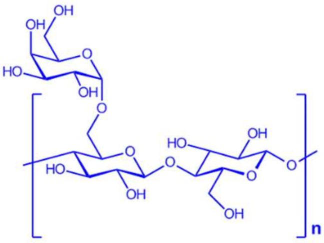
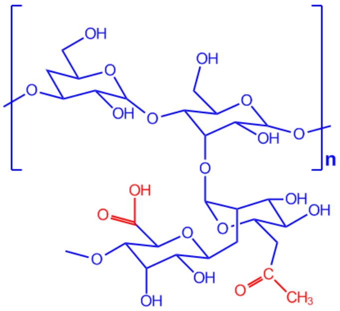
Biopolymers are known for their relatively cheap price compared to the synthetic polymers used as conventional coating materials, which depend greatly on the extraction and purification methods employed [64]. Biopolymers also have a number of other advantages: biodegradability in soil and nontoxicity [65,66], a good soil water-holding capacity, reduced oxidative stress, enhanced particle aggregation, and minimal soil erosion. Biopolymers can also be used directly as a soil amendment [67] and to stimulate the dormant microbial activity [68].

The most commonly used biopolymers with CRFs, their biomass origins and extraction methods and their chemical structures are presented in Table 1. Theses information are essential for choosing an adequate biopolymer, which depends on its availability, the extraction and purification method, and a number of key physicochemical properties that are useful in CRFs production. Some studies have reported that the release longevity of lignin, cellulose, and starch-coated fertilizers is too short [64]. Cellulose and starch are hydrophilic polymers due to the presence of hydroxyl groups (-OH) on their surface, and starch has poor mechanical properties. Lignin is comprised of heterogeneous biopolymers, it is insoluble in water, and it is incompatible with hydrophilic polymers such as chitin and cellulose, which are highly crystalline [1,69]. Overcoming such limitations is of considerable relevance, and these are the reason why, for biopolymers to be useful, they need to undergo a degree of chemical and physical modification. For instance, chitin can be modified by deacetylation, thereby converting it into chitosan [70], which has remarkable solubility and film-forming properties. Other researchers often incorporate crosslinkers [71–73], compatibilizers [20], and plasticizers [74–77] in the coating solutions. These added elements change the flexibility, tensile strength, and adhesion properties of polymeric membranes [74,77]. Blending and copolymerization of different biopolymers or biopolymers with synthetics has also become of interest, and these have been the subject of several studies. Researchers have tested various possibilities: natural rubber and starch [78], lignin and ethyl cellulose [79], starch with lignin [80], starch and polyvinyl alcohol [81,82], starch with poly(L-lactide) [83], sodium alginate and poly(acrylic acid-co-acrylamide) [84], starch and poly(acrylic acid-co-acrylamide) [85], chitosan with poly(acrylic acid) [86], guar gum and poly(acrylamidoglycolic acid) [87], starch and poly(vinyl acetate- co-butyl acrylate) [88], starch and poly(acrylic acid) [89], and sodium carboxymethyl cellulose with hydroxyethyl cellulose [90].

Table 1

The most commonly used biopolymers as coatings, their structure, origins, and some of the extraction methods

Biopolymer	**Structure**	**Origins**	**Extraction methods**
Alginate		-Brown algae	-Seaweed powders were treated many times with a 2% aqueous solution of $CaCl_2$, HCl 0.01M, pH 2, for 3 hours at 70 °C with mechanical stirring), centrifuged, solubilized in Na_2CO_3 (3%) and recovered after dialysis [91].
Pectin		- Primary cell walls and the middle lamella of higher plants (citrus peel, apple pomace, and sugar beet pulp) [92]	-Boiling of an aqueous solution of HNO_3 under various conditions in a heating mantle with a reflux system. After centrifugation (5000 rpm, 20 min, 4 °C), the supernatant was filtered and precipitated with absolute ethanol 1:2 (v/v) [93].
Cellulose		-Crop plants, wood, cotton, algae, and biomass wastes [94]	- Dispersion of dry powder in water at 2% (w/v). After centrifugation (2500 rpm, 30 min), a sodium hydroxide solution 4wt% was added to the resulting pellet (80 °C, 2 h, and 150 rpm). This treatment was repeated, and the sample was washed thoroughly with water, centrifuged, and then dried at room temperature [94].
Chitin		-Invertebrates (crustacean shells, insect cuticles…), fungi, green algae, cell walls, and yeasts [95]	-Chemical extraction comprising 3 steps: *Deproteination (0.125 to 5 M NaOH, at various temperatures and treatment duration. *Demineralization (0.55-1.5 M HCl, 35-50 °C, 30 min-6 h) * Discoloration (an organic solvent mixture or acetone to eliminate pigments) [96].
Chitosan			-Deacetylation of chitin (concentrated NaOH solution for a few hours) [96].
Lignin		-Lignocellulosic materials (agricultural residues, wood) [97]	-Fractionation process (ternary mixture solvent (methyl isobutyl ketone, ethanol, and water (25, 42, and 33% v/v) in the presence of H_2SO_4 0.025 M. The reaction was carried out at different temperatures (140, 160, 180 °C), 40 min, N_2 (20 bars), and 100 rpm. The reaction was stopped by quenching on ice (10 min), the mixture was then filtered and the solid fraction was washed with distilled water (neutralization to pH 6-7) [97].

Starch		-Maize, Wheat, Rice, Cassava [98]	-H_2SO_4 (0.15% w/w, 16 h at room temperature) followed by centrifugation (5000 rpm, 10 min), washed with anhydrous ethanol and acetone, and dried at 40 °C [98].
Carrageenan		-Red algae	-Seaweed was mixed with KOH (6% w/v), and the reaction was carried out at 80 °C for 3 h. The slurry was then filtered and the carrageenan in the permeate were precipitated with 80% isopropanol, filtered, and recovered by freeze-drying [99].
Guar gum		-Seeds	-Crushed seeds were immersed in NaCl solution (5%, pre-adjusted to pH 3 with acetic acid) for 24 h at 50 °C and 300 rpm. The mixture was sieved, treated with (90% ethanol and 10% isopropanol), centrifuged (6000 rpm, 7 min). The thereby obtained gum was then dissolved in clean water, precipitated with 90% ethanol and 10% isopropanol, filtered, and dried at 50 °C [100].
Xanthan gum		-Xanthomonas bacteria	-Fermentation of glucose by various species of Xanthomonas bacteria [101].

3.2. Slow-release mechanisms of CRF@BB

The nutrient release behavior and rate are the most important properties for CRFs. To test the release rate of nutrients from coated fertilizer, most authors have generally used water[102–106], soil [107,108] or both systems [109,110], while a small number have used saline solutions [111]. Most researchers choose distilled water as the environment for release testing. This is related to the large differences encountered in regard to soil properties and climate conditions. Therefore, they typically use distilled water, which is a valid and readily available release environment for comparing results. However, the release behavior in water is not similar to that in soil. Vudjung et al. [63] claimed that coated urea released 100% of nitrogen within 24 days in soil, whereas the release rate of nitrogen in water was very fast (100% in 3 days). El Assimi et al. [109] and Baki et al. [112] have confirmed this result. According to

Baki, the release rate of nitrogen through the coated fertilizer was lower in soil than water; approximately 60% were released in soil after 30 days, while in water, approximately 35% were released within 10 days. This result is not in keeping with the results reported by Jia et al. [113]. These authors showed that the release rates of P_2O_5, Cu, and K_2O through coated fertilizer in soil were slower than in water, whereas the release rate of nitrogen was faster in soil than water. This complexity and heterogeneity of the different studies regarding the release of NPK (in water, soil, etc.) complicates the determination of the release mechanisms. However, several researchers claim to have identified and understood the controlled-release mechanism from coated fertilizers at different stages. It is not easy to establish the mechanism of release, which depends on many factors: the coating and soil properties. In this section, we do not discuss coated fertilizer/soil interactions. Rather, we focus only on the release mechanisms of nutrients through the polymeric coating materials in water and in soil solutions. Morgan [114] reported that polymer-coated materials release nutrients by diffusion through a semi-impermeable membrane. Shaviv [27] and Liu [115] developed a now well-known model called the "multi-stage diffusion model", in water. According to this model, the coated fertilizer has to come into contact with water in order to liberate its nutrients. In the first stage of the release process, the water penetrates through the coating membrane and it condenses on the solid core, which is followed by partial nutrient dissolution. Due to this dissolution, internal pressure (or osmotic pressure) builds up in the granule, which then swells up. Two phenomena may take place as a function of the membrane resistance and the internal pressure. If the membrane resists the osmotic pressure, the core fertilizer releases slowly by diffusion, which is called the diffusion mechanism, and it is determined by the concentration gradient across the coating, or by the pressure gradient, or by both gradients. However, if the internal pressure surpasses the membrane resistance, the "failure mechanism" or "catastrophic release" occurs, whereby the entire content is released due to rupture of the coating material followed by bursting of the granule (Fig.4). Catastrophic release usually occurs with frail and non-elastic coatings such as sulfur-based coatings. Moreover, biopolymer-coated fertilizers are known for their slow-release mechanism [116]. Interactions between the fertilizer granule and the polymer layer are physical rather than chemical [117]. Wu et al. [5] proposed a model of the release mechanisms of nutrients in soil from polymeric coated fertilizers, especially from double-coated fertilizers with a superabsorbent outer coating. In the first step, the layer slowly swells by the soil solution and then transforms into a hydrogel. A dynamic exchange between the free water in the hydrogel and the water in the soil occurs, after which the free water in the superabsorbent layer migrates to the middle layer, and water then slowly penetrates through the inner coating in the initial stage and compounds in the fertilizer become dissolved. In this stage, diffusion is the rate-limiting step in the release. Under the effect of water, ions, and microorganisms present in the soil, the middle layer slowly degrades in the last stage and the nutrients continue to dissolve. In this stage, the degradation rate determines the nutrient release rate. Finally, the dissolved fertilizer components diffuse out of the middle layer and enter into the outer layer so that they are then released into the soil by the dynamic exchange of free water.

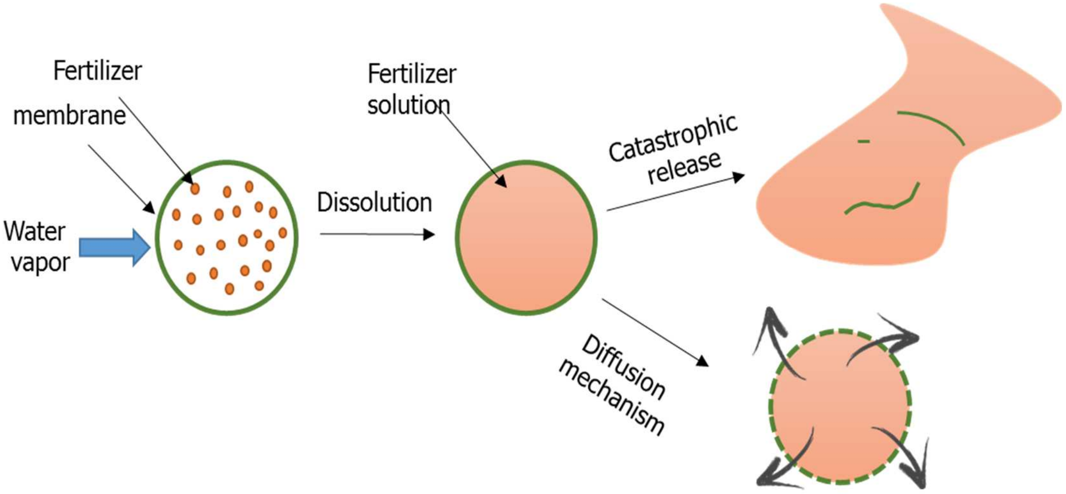


Fig.4. Release mechanisms of nutrients through a polymeric coating when in contact with water (or soil solution)

3.3. Coating parameters that control nutrient release

There are many factors that affect the release rate of nutrients through these polymer-based coatings. The most important parameters are: 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 (Table 2). All of these parameters influence the thickness and the porosity of the coating layer [118]. These parameters are interdependent and govern the nutrient release rate [19,20,74,118–120]. They are discussed in detail below.

3.3.1. Coating methods

The coatings of granular fertilizers can be applied by various methods such as spraying of a liquid, dipping into a liquid, precipitation from supercritical fluids, or by deposition of a powder using an electrostatic technique [121]. The most commonly used techniques for coating fertilizers are: immersion and spraying a liquid onto the substrate (Fig.5). Spraying is commonly carried out either in a coating pan (rotary drum) or a fluid bed coater [122].

Immersion: realizes by dipping the fertilizer into the polymer coating solution [2,123]. The solution adheres to the granule surface of fertilizers and fixed by a drying system.

Coating pan: This is one of the most commonly used techniques to coat fertilizer granules with polymeric solutions. The coating liquid is transferred as a spray to the surface of the beads already present in the spray zone. The system employs an air-atomizing spray nozzle at the center of the drum to spray the coating solution and a hot air stream to evaporate the solvent and then dry the coated particles. The coating is carried out by two systems; the first one is a cascading layer composed of a thin layer of granules that flows down the free surface, and the second one is a quasi-static zone comprised of the remaining granules that rotates as a fixed bed. As the pan rotates, the beads cascade through the spray zone under gravitational force. The granules come into contact with the spray and they become coated with the coating solution, followed by drying, before moving into the bulk of the tablet bed. After a period of circulation, the beads may re-enter the spray zone and the coating and drying process are repeated. The granule residence time at the surface of the cascading bed determines the quantity of solution received by a granule per pass through the spray zone. The quality and performance of a coating are influenced by several parameters: simultaneous exchanges of heat and mass between the coater pan and the inlet air stream, the spraying material and substrate, the dimensions, the rotational speed, the configuration and the number of baffles, pan loading, the bed humidity, and the pan coater temperature [124,125]

Fluidized bed (Wurster): This is used to coat solid granules such as pellets, granules, or powders. It is widely used in the pharmaceutical, food, feed, and fertilizer industries [126]. Fluidized beds are based on the fluidization of the initial granules by hot air, while a suspension or solutions are sprayed onto them. There are three commonly used configurations of fluidized bed; top spray, bottom spray, and side spray. In regard to the coating of fertilizers, a Wurster fluidized bed, which is a modified bottom-spray fluidized bed, is the most suitable apparatus to coat fertilizers. This configuration is characterized by a bottom-spray nozzle and a Wurster tube located in the center. Due to this special design, the granules are forced to follow a circulating flow trajectory [127,128]. The key variables that control this coating process are classified according to three aspects; the first one relates to fluidization, which is controlled by the input air flow rate, the dimensions and type of the equipment, the particle size and density, the substrate surface characteristics, and the batch size. The second one relates to the coating. It is determined by the position and the design of the nozzle, the droplet size, the viscosity, the surface tension and density, the injection pressure, atomizing air, as well as the coating liquid flow rate. The third aspect comprises the drying parameters, including the inlet and outlet temperature, as well as inlet air flow rate and the air humidity [129,130].

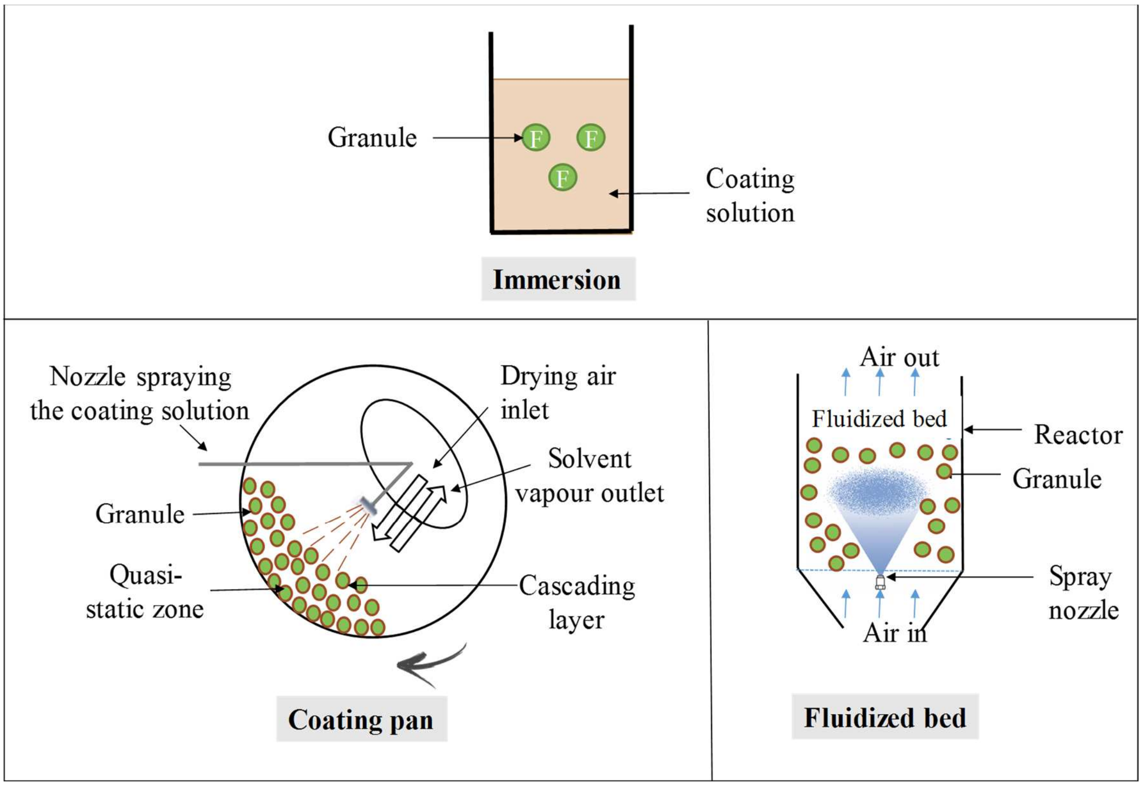


Fig.5. The most commonly used techniques for coating fertilizer granules

The coating methods affect the quality of coatings, which is a key parameter to control the nutrients release behavior. With immersion, the fertilizer granules can be partially dissolved because they are dipped into the coating solution, especially water-soluble fertilizers. The granules can also stick to each other if the solution is very viscous and the coating is generally damaged when they are separated after drying. Use of the rotating pan method is a good alternative for immersion. The coating parameters for a rotating pan impact the coating quality (dimensions, rotational speed, spray flow rate, etc.). Generally, the rotating pan method minimizes mechanical damage of the beads and it reduces the level of attrition because the granules are moved in a gentle manner. Consequently, the coated layer is damaged less by the coating process. However, it is not easy to achieve a uniform thickness for the coated layer for the entire fertilizer batch unless large amounts of the coating materials are used. The limited coating uniformity and the higher product variability affect the nutrient release rate. The release will not be uniform through the coating of the granules [121,122,126,131]. With the fluidized bed method, the layer thickness is uniform, with a precise degree of film coating. Nevertheless, aggressive granule movement results in a high level of mechanical stress on the beads, and the attrition can affect the quality of the coatings and consequently the release behavior through these coatings [5,121,131,132].

3.3.2. Coating formulation properties

Formulation is a key parameter that governs the release behavior of nutrients. It depends on the components and their compatibility, their hydrophilic or hydrophobic nature, and their concentrations in the solution and the viscosity.

Hydrophobicity: The hydrophobic/hydrophilic nature of the formulations used in the preparation of the coating is a crucial parameter for the release behavior of nutrients. When the coating material is hydrophobic, the affinity between the layer and water is weak. This lack of affinity prevents the penetration of large quantities of water into the fertilizer core and it decreases the dissolution [19]. Jarosiewicz et al. [19] showed that the release rate of NH_4^+ is three times faster when hydrophilic polyacrylonitrile is used as the coating for nitrogen fertilizer compared to hydrophobic polysulfone.

Component compatibility and modifying agents**:** The compatibility between components affects the coat-forming quality. If the components are not compatible, two or more phases could arise in the same coating, which would result in a non-homogeneous film that could exhibit cracks and pinholes. In most coating formulations; plasticizers, crosslinkers, or compatibilizers are added to improve the mechanical and adhesion properties of polymeric membranes [74,77,133]. When these properties are adequate, the shell can resist the internal pressure created inside the core in contact with water, and the nutrients are then released slowly without the shell being destroyed. Niu et al. [134] reported that the presence of plasticizers slows the release of ammonium nitrate. They suggest that this is related to the formation of films without cracks when plasticizers are added, which decrease the permeability of water and slows the release of nutrients. Blending, grafting, and copolymerization of different biopolymers, or biopolymers with synthetics, are also used to produce good coatings. Coating of urea with natural rubber reinforced by grafting with modified cassava starch (NR-g-ST) has been reported by Riyajan et al. [120]. Capsule coating with only starch resulted in almost 100% N release within 8 h. With the NR-g-ST coating, the capsule N release was only 21% within 1 day. This decrease in the N diffusion rate could be related to the chemical interaction between natural rubber and starch via grafting interaction.

Polymer concentration*:* The release rate of nutrients also decreases as the polymer concentration in the coating solution is increased. Indeed, higher polymer concentrations result in a greater thickness and lower porosity in the coating layers of fertilizer granules. Nui et al. [134] showed that coating formulations with 10% ethyl cellulose in the coating solution produce layers on coated urea that are less thick (49 µm) compared to 70 µm with 20%. The release of N through the thick layer was slower than for the thin layer. These results are in good agreement with those of Pérez et al. [135] who argued that the release of N from an ethyl cellulose-coated granule depends on the polymer concentration in the formulation. As expected, a high concentration of polymer increased the thickness of the coating film and slowed the release of N. The polymer type and its concentration also affect the porosity of the coating. The coatings formed from solutions with a higher polymer concentration exhibited reduced porosity [19], and consequently the release rate of nutrients decreased.

Viscosity: Solution viscosities that are too low or too high can result in an incomplete or damaged coating layer, or they can induce dissolution of water-soluble fertilizers in case of solutions with very low viscosities. Jarosiewicz et al. [19] reported that the viscosity of film-forming solutions increases as the polymer concentration increases. This causes an increase in the thickness and a decrease in the porosity as well as in the release rate of nutrients.

3.3.3. Number of coating layers

Fertilizer granules can be coated by one [136] or several layers [137,138] using the same coating solution. They can also be coated by two [109,138–141] or three layers [142] of different solutions, and by the same or different coating techniques. Single and double layers are the most common. In the case of double and triple layers, the second layer is generally superabsorbent.

NPK granules with a single coating: A single layer is made using one of the techniques mentioned in Section 3.3.1. Multiple layers are obtained by coating the fertilizer granule and drying it before re-coating until the desired number of layers is obtained. Generally, multiple layers using the same solution are obtained using the immersion technique. The granules are dipped once, twice, or several times in the same coating solution. Messa et al. [143] developed a chitosan-based formulation to coat NPK fertilizer with a single coating. They found the chitosan coating provided a reduction in the initial release rate of NPK, 100% of NPK was released in water from coated fertilizer within 2 hours compared to 100% within less than 20 min from uncoated fertilizer. Ahmed et al. [144] also prepared a chitosan-coated phosphorus fertilizer, but they studied the effect of the number of layers on the release rate of P. Compared to a single layer (63 µm) of coating film, the thickness of the double and triple-coated films was approximately 1.5 (96 μm) and 2 (128 μm) times higher, respectively. The average thickness of the coating film increased as the number of coatings increased. The release rate of P was lower with the triple-coated granules than with the single-coated granules, thus revealing the effect of thickness on the P release behavior. Jarosiewicz et al. [19,119] also reported that coated NPK granular fertilizer based on cellulose acetate and a modifying agent (formamide) released nutrients rapidly after 5 h and that the slowest release of macroelements was achieved with a double coating of 18% polymer solution with 5% formamide in the casting solution. They showed that NPK coated with a single layer of 17% polyacrylonitrile solution released 97.3% of the K compared only to 11.7% with three layers of the same solution.

NPK granules with double coatings: For double layers with different coating solutions, the aim is to ensure several properties using multiple layers. The first layer is generally intended as a physical barrier to impede the release of nutrients, and the second layer is a superabsorbent entity capable of absorbing water and releasing it when the plant needs it. These are multifunctional fertilizers that are particularly useful in arid zones. The multiple layers increase the coating thickness and decrease its porosity as well as the release rate due to a more compact structure of the coating and a lower porosity compared to a single coating [19]. Wi et al. [145] developed a double-coated slow-release NPK compound fertilizer with chitosan as the first layer and poly(acrylic acid)/diatomite – containing urea – as the superabsorbent second layer. The release rate of N, P, and K through this coated fertilizer was in the range of 2.3-11.9% in 3 days and 64-73.2 % in 30 days. These release rates are much slower than that of uncoated fertilizer, which released more than 80% and 87% within only 2 and 5 days, respectively. Ni et al. [146] developed a multifunctional slow-release fertilizer using a matrix of NPK fertilizer with natural attapulgite clay as the core, sodium alginate as the first layer, and sodium alginate grafted to poly(acrylic acid-co-acrylamide)/humic acid superabsorbent polymer as the second layer. The release rate of N from the untreated fertilizer in soil was 98.5% in 12 h [147], while the same percentage was released through the coated fertilizer in 30 days. Xie et al. [28] reported a double-coated slow-release NP fertilizer with a wheat straw/sodium alginate blend as the inner coating and poly(acrylic acid-co-N-hydroxymethyl acrylamide)/wheat straw superabsorbent composite as the outer coating. The release of N from the coated fertilizer in soil was less than half (40.3%) of the release rate of the untreated fertilizer. The release of P was only 42.6% in 30 days from the coated NP compared to 66.2% in 5 days from the uncoated fertilizer. Wang et al. [148] developed a multifunctional N slow-release fertilizer by coating granules of nitrogen using k-carrageenan-sodium alginate (k-SA) and cross-linked k-carrageenan grafted to poly(acrylic acid)/celite superabsorbent as the inner and outer coating materials, respectively. The release rate of nitrogen from the coated fertilizer was 94% within 25 days, which was much slower than the uncoated nitrogen fertilizer, which was reported to release 98.5% of the N in 12 h [147]. The same authors have developed a slow-release fertilizer (NPK) based on natural attapulgite clay as a matrix, guar gum as an inner coating, and guar gum grafted to poly(itaconic acid-co-acrylamide)/humic acid superabsorbent polymer as an outer coating. The release rates for N, P, and K through the core (NPK +attapulgite) in soil were fast; 100% in 5 days for N, and 93.3% and 94.2%, for P and K, respectively, in 30 days, while the release rates through the double-coated fertilizer were 100% in 20 days for N, and 88.2% and 92.4% for P and K, respectively, in 30 days. Of note, the release rate of nitrogen was the highest, while the release rate of P was the slowest, which is in agreement with the findings of Wu et al. [5]. To explain this, the ionic mobility and the electronic and steric effects of K^+ and NH_4^+ ions were compared. The ionic mobility of NH_4^+ and K^+ are very similar (1.000 and 1.001 $m^2\ s^{-1}\ V^{-1}$), and they also have the same positive charge value. However, the size of K^+ (1.33 Å) is smaller than that of $NH4^+$ (1.47 Å), and K^+ ions have a higher surface area charge density to interact with the negatively charged carboxylate ion of the hydrogel layer [142] and hence spread more slowly [5]. Lü et al. [77] investigated an environmentally friendly entity of N mixed with natural attapulgite as the core, starch acetate as the inner coating, and carboxymethyl starch/xanthan as the outer coating. The release rate from the uncoated fertilizer was 79.9% in 1 day, while it decreased to 56.5% by coating the fertilizer with starch acetate only. Addition of the second layer (carboxymethyl starch/xanthan gum) doubled the time taken to release 100% of the N from five to ten days. Wang et al. [149] developed a biomass-based multifunctional controlled-release fertilizer. This fertilizer was based on natural attapulgite, ammonium zinc phosphate, and urea, while cellulose acetate butyrate (CAB) and carboxymethyl chitosan-g-poly(acrylic acid)/attapulgite superabsorbent composite were the inner and the outer coating, respectively. The release rate of N by the untreated fertilizer in soil was 98.5% in 24 h. After coating, 9.2, 53.1, and 81.4% of the N was released within 3, 15, and 30 days, respectively. The release of Zn from the coated fertilizer was lower than N; only 41.2% of the Zn was released within 30 days. Mingyo et al. [150] reported the production of a slow-release membrane-urea fertilizer. The first layer was starch and the second layer was acrylic acid and acrylamide. The release rate of N in soil from just the fertilizer was more than 85% in 2 days. However, when the fertilizer was coated with starch and acrylamide, the release rate decreased more than 8-fold.

NPK granules with triple coatings: Triple coating of fertilizer is achieved by coating the core using the first solution, and then waiting for it to dry before applying the second followed by the third coating solution. However, only a limited number of studies have been undertaken using three layers from different coating solutions. Noppakundilograt et al. [142] developed a trilayered controlled-release NPK fertilizer hydrogel by dipping the NPK fertilizer granules into poly(vinyl alcohol) (PVA) to form the first layer. After drying, the PVA-coated fertilizer granules were immersed in a chitosan solution and the PVA-chitosan bilayer-coated fertilizer granules were then crosslinked in a closed system for 4 days. After this, the third layer was prepared by suspension graft copolymerization of acrylic acid (AA) and acrylamide (AM) to form poly(AA-co-AM). The results show that the coated NPK fertilizer did not fully dissolved in water within 30 days and that the total N release was the highest (83.9%) compared to P (62.3%) and K (36.2%).

Table 2

Fertilizers type, coating materials used, operating conditions and parameters of coating, and nutrient release rates

Reference	Coating materials	Fertilizer	Granule size (mm)	T coating (°C)	Contact time (min)	T drying (°C)	Drying time (min)	Coating method	Thickness (mm)	Release rate (%)
[63]	Natural rubber (NR)/Starch (ST)/ Wax (W)	N	3.6	100/Room temp	-	-	-	Rotary drum coater	0.108-0.193	* In water: - Urea beads: 100% in 2h - W/NR/ST blends: 100% in 72 h * In soil: - Urea beads: 100% in 72h - W/NR/ST blends: 100% in 576 h
[151]	Starch acetate/ glycerol/ polyvinyl alcohol biocomposites (SA/Gly/PVA)	Diammonium Phosphate (DAP)	-	90	-	60	240	Immersion	0.045-0.095	Nitrogen and phosphorus release: *In water: - Uncoated DAP: 100% of N in 1h35 and 100of P in 1h20. -SA/Gly/PV- coated DAP (Single layer): 100% of N in 3h50 and 100% of P in 3h20. -SA/Gly/PV- coated DAP (Double layer): 100% of N in 5h and 100% of P in 4h30.
[109]	Chitosan-clay composite/Paraffin wax	DAP	2-4	50	-	Room temp	-	Immersion	0.02-0.06	Phosphorus release: * In water: - Uncoated DAP: 100% in 2h - Chitosan-clay/ Paraffin wax: 100% in 16h * In soil: - Uncoated DAP: 100% in 576h - Chitosan-clay/ Paraffin wax: 40% in 720h
[152]	Ethyl cellulose/cellulose-based superabsorbent	N	2-3	-	-	50	-	Rotating pan	-	Nitrogen release: * In soil: -Uncoated urea: 97% in 96h -Coated urea: 0.2, 15.1 and 58.6% in 96, 168 and 360h, respectively.
[153]	Ethyl cellulose	NPK	4-5	-	-	60	-	Immersion	0.204-0.244	Phosphorus release: * In water: - Uncoated NPK: 100% in 1h - Ethyl cellulose-coated NPK: 75% in 672h.
[56]	Chitosan (CS)/Graphene Oxide (GO) nanocomposites	KNO_3	-	-	-	Air-drying	Overnight	Immersion	-	Potassium release: * In water: - Uncoated KNO_3: 100% in 10min - CS-coated KNO_3: 14% in 48h - Cs-GO-coated KNO_3: 10% in 48h

[143]	Chitosan (CS)/Nanocellulose microparticles	NPK	0.002	95-180	-	Air flow	-	Spray dryer	0.563-0.682	* In water: -Uncoated NPK: 100% in < 20min -CS-coated NPK: 100% in 2h -CS/Nanocellulose-coated NPK: 100% in 5h
[138]	Poly (acrylic acid)-g-natural rubber NR-g-PAA	Urea/KH_2PO_4	1.3-1.5	-	-	-	-	Rotating pan/ Shaking with powder (Water atomization)	0.5	* In soil: -Uncoated fertilizer: 100% in 120h - NR-coated fertilizer: 69.44% of **N**, 69.28% of **P** and 66.94 of **K** in 720h. - NR-g-PAA coated fertilizer: 54.35% of **N**, 51.18 of **P** and 44.37% of **K** in 720h
[154]	Coco peat fibers-grafted-poly (acrylic acid) hydrogel	NPK	Dissolved in deionized water	60	-	60	Until constant weight	In-situ solution polymerization	-	* In water: - Uncoated NPK: 100% in 1h45 - Coco peat fibers-g-PAA-coated NPK: 38.1% in 3h and 100% in 840h (5weeks).
[53]	Sulfonated carboxymethylcellulose-g-Poly (AA)/ Polyvinylpyrrolidone/ Silica SCMC-g-PAA/ PVP/Silica	NPK	Dissolved in SCMC solution	60	4h	70	1440	In-situ polymerization	-	*In water: - Uncoated NPK: 100% in 6h -SCMC-g-PAA coated NPK: 89% in 1 month - SCMC-g-PAA/PVP coated NPK: 75.3% in 1month - SCMC-g-PAA/PVP/Silica coated NPK: 65.3% in 1month * In soil: Uncoated NPK: 100% in 4h -SCMC-g-PAA coated NPK: 83.6% in 1 month - SCMC-g-PAA/PVP coated NPK: 72.3% in 1month - SCMC-g-PAA/PVP/Silica coated NPK: 54.6% in 1month
[155,156]	Lignin/Carrageenan (LC)	Triple superphosphate (TSP)	2-3	-	-	65	-	Rotating pan	0.218 ± 0.062	Phosphorus release in water: - Lignin/Carrageenan-coated TSP: 56% in 48h
	LC/Polyethylene glycol 200									LC/PEG200-coated TSP: 65% in 48h
	LC/Polyethylene glycol									LC/PEG2000-coated TSP: 79% in 48h

	2000									
	LC/Glycerol									LC/Gly-coated TSP: 71% in 48h
[116]	Lignin	Triple superphosphate (TSP)	2-3	-	-	65	-	Rotating pan	0.0713± 0.0236	Phosphorus release in water: -Uncoated TSP: 99.5% in 72h - Lignin-coated TSP: 76% in 120h
	Alginate									- Alginate-coated TSP: 75.3% in 120h
	Carboxymethyl cellulose									- Carboxymethyl cellulose-coated TSP: 73.7% in 120h
	Carrageenan									- Carrageenan-coated TSP: 90.2% in 120h
	Lignin/ Alginate									- Lignin/ Alginate-coated TSP: 64.9% in 120h
	Lignin/ Carboxymethyl cellulose									- Lignin/ Carboxymethyl cellulose- coated TSP: 59.2% in 120h
	Lignin/ Carrageenan									- Lignin/Carrageenan-coated TSP: 75.3% in 120
[52]	Lignin/montmorillonite (L/MMT)	Urea	Extruded urea/MMT (1-2 mm)	135	15	Room temp	-	Immersion	-	Nitrogen release: * In water: -Uncoated urea: 100% of N in 1h. -L/MMT-coated urea: 34.6% of N in 105h. *In soil: -Uncoated urea: 100% in 30 days. -L/MMT-coated urea: 61.6% of N in 30 days.
[157]	Cellulose-g-poly(acrylamide)	Urea	Dissolved in water	80	-	80	300	Copolymerization	-	Nitrogen release: *In water: - CMC-g-PAM: 96% in 83 days. - CMC-g-PAM/ MMT (2.7, 5, 10 and 14.4 wt% MMT): 86.3, 78.8, 74.28 and 70.2% in 83 days, respectively.
	Cellulose-g-poly(acrylamide)/ Montmorillonite									
[158]	Dolomite-Alginate (DA)	KH_2PO_4	P-loaded DA beads	-	3h	100	-	Injected dropwise ($CaCl_2$ atomization)	-	Phosphorus release: * In water: - DA-coated KH_2PO_4: 40% in 10 days and about 90% in 60 days.
[112]	Alginate-g-poly (acrylic acid-co-acrylamide)/ Biochar	NPK	Loaded in the graft copolymers	80	-	50	Overnight	Graft copolymerization	-	N, P and K release: * In water: - Coated-NPK: 35% of N, 60% of P and 62% of K in 10 days.

										* In soil: -Coated-NPK: 60% of N, 30% of P and 30% of K in 30 days.
[159]	Sodium alginate-g-poly (acrylic acid-co-2-hydroxyethyl methacrylate)/ Montmorillonite	Urea	Dissolved in water	-	24	60	-	Loaded onto Alg-g-P(AA-co-HEMA)/MMT in aqueous solution	-	* In water: - Alg-g-P(AA-co-HEMA)/MMT (5%)-coated urea: 30% in 80 days. - Alg-g-P(AA-co-HEMA)/MMT (10%)-coated urea: 50% in 80 days.
[160]	Chitosan/alginate composites Gelatin/alginate composites	Urea	Dissolved in composite solution	-	2	Air flow	-	Urea-entrapped beads	-	Nitrogen release: * In water: - Chitosan/alginate-coated urea: 10% in 3h and 14% in 5h. - Chitosan/gelatin-coated urea: 6% in 3h and 8% in 5h.
[161]	Poly(ε-caprolactone)-g-Guar Gum and Poly(ε-caprolactone)-g-Halloysite Nanotubes	DAP	4	-	-	30	-	Immersion	0.025	Nitrogen and phosphorus release: * In water: - Uncoated DAP: 100% in 1.5h -PCL-g-GG (1%) coated DAP: 100% of N in 45h and 100% of P in 35h -PCL-g-HNT (1%) coated DAP: 100% of N in 50h and 100% of P in 52h
[47]	Polyvinyl Alcohol/Polylactic Acid core/shell fibers (PVA/PLA)	NPK	Dissolved in composite solution	90	-	-	-	Co-axial electrospinning	-	* In water: -NPK-loaded PVA/PLA core/shell fibers: 60% in 3 days, 80% in 28 days and 90% in 90 days. -NPK-loaded PVA fibers: 60ù in 10 days and 70% in 20 days.
[162]	Polylactic acid/Cellulose acetate PLA/CA Polylactic acid/Cellulose acetate/ nano-SiO_2 PLA/CA/SiO_2 Polylactic acid/Cellulose acetate/ Polyethylene glycol PLA/CA/PEG	Urea	~5	-	40	50	60	Immersion (phase inversion)	0.1-0.2	* In water: -PLA/CA-coated urea: 50% in 150 days and 100% in 650 days. -PLA/CA/SIO2 and PLA/CA/PEG-coated urea: 50% in 50 days and 100% in 150 days.

[163]	Hydroxymethylated lignin/Phenol-formaldehyde/ Talc (HML/PF/T)	Superphosphate	-	120	-	-	-	Rotating pan	-	Phosphorus release: * In water: -Uncoated superphosphate: 70% in 3 days. - HML/PF/T-coated superphosphate: 15% in 3 days.
[164]	Carboxymethyl cellulose/β-cyclodextrin-based microspheres (CMC/ β-CD)	Urea	-	40	360	-	-	Graft copolymerization	-	Nitrogen release: * In water: -Uncoated urea: 100% in 24h. - CMC/ β-CD -coated urea: 21.24% in 24h and 95.75% in 1 week.
[165]	k-Carrageenan/Glycerol	NPK	-	-	-	-	-	Immersion	-	* In water: -k-Carrageenan/Glycerol-coated NPK: 17% of NH_4^+ in 1h and 95% in 28 days, 23% of NO_3^- in 24h and 68% in 28 days, 1.8% of PO_4^{3-} in 10 mon and 62% in 28 days.
[108]	k-Carrageenan/Sodium Alginate/ Carboxymethyl Cellulose Hydrogel Blends NaAlg/KC/CMC	NPK	Dissolved in blend solution	-	-	-	-	Hydrogels through ionic crosslinking	-	* In soil: - NaAlg/KC/CMC-coated NPK: 53% in 3 days.
[166]	Bio-based amino-oil (Priamine)	DAP	2-4	-	-	60	-	Rotating pan	0.065 (single layer) 0.085 (double layer)	Phosphorus release: * In water: -Uncoated DAP: 100% of P in 2h. -Priamine-coated DAP: 100% of P in 98h (single layer) and 100% in 126h (double layer).

4. Effects of CRF@BB on soil & plant

Over the last decades, various polymers have been widely used and have been found very promising for agricultural application. Most work involving polymers coated fertilizers focuses on the rate of nutrient release to water or soil (Table 2). However, papers investigated the combination effect of polymer/biopolymers and fertilizers (CRFs@BB) on soil properties and plant growth are scare, and the work existing does not give details of the formulations and the polymers used. In this part, these works will be synthesized and the effect on some soil properties as well as on plant will be presented.

4.1. Effect of CRF@BB on soil properties

4.1.1. Effect of CRF@BB on the soil pH

The soil pH is an important parameter for plant growth because it affects the availability of nutrient. Most nutrients are available to the plant roots in a soil pH of 5.5–7. Wang et al. [149] prepared a biomass-based CRF comprising urea granules, co-granulated with natural attapulgite and ammonium zinc phosphate as a fertilizer core, cellulose acetate butyrate as an inner coating, and carboxymethyl chitosan-g-poly(acrylic acid)/attapulgite hydrogel as an outer coating. The developed superabsorbent served as outer coating was immersed in a soil solution with pH values from 4 to 10 (adjusted with HCl or NaOH aqueous solution). Results showed that the superabsorbent-based biopolymers not only absorbed water to enhance plants survival in arid conditions, but also buffered the soil acidity or alkalinity to a pH of approximately 7. This is because of the large amounts of -COOH and -COO− that can react with the OH^- and H^+, respectively, of soil solution. Another similar work was carried out by Boli et al. [167] using co-granulated beads based on urea, monopotassium phosphate and natural attapulgite clay as a core, guar gum as an inner coating, and guar gum-g-poly itaconic acid-co-acrylamide)/humic acid superabsorbent polymer as an outer coating. Investigations showed that the superabsorbent buffered the soil solution to a pH of 7.09–7.3 from initial pH values that varied from 4 to 10.

4.1.2. Effect of CRF@BB on the soil microbial biomass

Soil microorganisms mediate many important biological processes for sustainable agriculture. They contribute in nutrient cycling, the degradation of agrochemicals and pollutants, etc. Soil microorganisms depend on soil organic C for energy and cell synthesis. The addition of carbon-rich polymers can stimulate microorganisms. There have been few studies to date using biopolymers/polymers as coatings, and all of them involved polymer-coated N fertilizers without revealing the nature of the polymer that was used. This is probably because they use commercial coated fertilizers with confidential formulations. Zhang et al. [168] showed that a polymer-coated controlled-release urea increased the microbial biomass C and the functional diversity of bacteria more than urea at the majority of the study sites. This probably means that the nitrogen as well as the C contained in the coated urea was assimilated by the microorganims. The microbial metabolic quotient qCO2 was higher for the control treatment (without fertilizer), because soil microorganisms were probably nutritionally stressed. Another work carried out by Nardi et al. [169] reported the effect of a polymer-coated urea on soil microbial biomass. They observed a higher microbial biomass C content in soil treated with CRFs than untreated soil. However, the soil microbial biomass N content with slow-release urea fertilizers was lower during the seedling stage than control treatment, but was higher after seedling stage. Inubushi et al. [170] also reported that the soil microbial biomass N was higher with conventional urea fertilizer than polymer-coated fertilizer. As to Chu et al. [171], they reported that controlled release urea did not significantly affect the microbial biomass, but had significant effects on soil microbial activities (dehydrogenase activity). This result is in accordance with the findings of Acquaye et al. [172] who reported that thermoplastic polyolefin-coated urea did not affect the amount of microbial biomass N.

4.1.3. Effect of CRF@BB on nutrients bioavailability

The coating serves as a protective layer to make soil-fertilizer contact difficult and limit interactions between the soil and the nutrients (e.g. phosphorus fixation). The nutrient availability can be governed by the nutrient release. There have only been a few studies to date that investigated the effect of CRF@BB on the availability of nutrients in soil. Garcia et al. [173] reported that lignin-coated TSP and rosin-coated DAP increased the P availability in calcareous soils and reduced P fixation. Diez et al. [174] also reported that rosin-coated DAPs provide control of P fixation in calcareous soils and that the P remains available for long periods. McKenzie et al. [175] reported that there was no difference between coated urea and uncoated urea in terms of N uptake, while Inubushi et al. [170] observed that coated fertilizer induced more N uptake by rice plants and a higher N fertilizer recovery rate than conventional fertilizer. Zhang et al. [176] reported that controlled-release urea reduced the potential N loss compared to urea.

Cruz et al. [177] studied the effect of polyurethane-coated DAP fertilizer on P availability in an oxisol. They argued that the thickness of the coating affects P availability. According to the same authors, non-coated or DAP with a thin coat decreased the P availability due to high P adsorption by the soil colloids, while DAP with a thicker coat increased the available P due to its slow release and the shorter contact time of P with the soil.

Castro et al. [178] compared the migration of P in soil at 63% WHC through uncoated MAP and polymer-coated MAP in an oxisol (pH between 5.2 and 7). The distribution pattern of P with the two treatments was not significantly different. The majority of the P from MAP and the coated MAP (> 80%) remained within 0–7.5 mm from the point of application and the remaining P did not migrate beyond a 25.5 mm radius of the fertilizer granule. Lombi et al. [179] and Lawton et al. [180] found the same diffusion radius for P using different P sources (MAP, DAP, TSP, and others) in different water-saturated soils (calcareous, oxisol, and loamy soils).

4.1.4. Effect of CRF@BB on the water holding capacity and water retention

Several researches are carried out to evaluate the biopolymers effect on soil physical properties. In this sense, Montesano et al. [181] studied the effect of cellulose-based superabsorbent hydrogels on the water retention properties of the soil. They showed that cellulose dramatically improve water retention and water holding capacity of a sandy soil and perlite (soilless substrate). Similar results have been reported by Tran et al. [182] who suggested that the addition of biopolymers (starch and xanthan gum hydrogels) significantly improve the water holding capacity in sandy soils. This highest amount of water retained can be explained by hydrophilic groups and network structure in biopolymer and by the formation of strong hydrogen bonding between water molecules and these biopolymers. Soils treated with biopolymer-coated fertilizers and/or superabsorbent-coated fertilizers also enhance the water retention and water holding capacity of the soil. The water-holding capacity and the water retention of soils with coated fertilizers always exceed those of soils with uncoated fertilizers. Table 3 summarizes the results of some of the studies to date.

Table 3

Comparison between the water-holding capacity (WHC) and the water retention (WR) of soil in the presence/absence of coating

	WHC (%)		**WR (wt%)** (1-Water evaporation (wt%))	
	Without Coating	**With Coating**	**Without Coating**	**With Coating**
[183]	28.2	40.8	7% after 10 days 0% after 20 days	23.7% after 10 days 14% after 20 days
[184]	41.5	54	0 after 4 weeks	30.8% after 2 weeks
[185]	28.17	40.26	10.4% after 10 days 2.1% after 20 days 0% after 30 days	25.1% after 10 days 13.2% after 20 days 3.9% after 30 days
[5]	30.17	40.35	12.4% after 10 days 2.6% after 20 days 0% after 30 days	24.7% after 10 days 15.5% after 20 days 7.8% after 30 days
[148]	-	59	- 0% after 10 days	113.5% after 0days 62% after 10 days
[145]	29.08	39.76	44% after 15 days 5.5% after 30 days	56.5% after 15 days 22% after 30 days
[149]	38.5	69	5.1% after 15 days 0% after 18 days	49.8% after 15 days 44.1% after 18 days
[150]	29.35	41.8	49% after 12 days 5% after 21 days	64.5% after 12 days 27% after 21 days
[186]	33.1	46.8	41% after 15 days 6.5% after 30 days	65.6% after 15 days 24.8% after 30 days

4.2. Effect of CRF@BB on plant growth

Over their undeniable role in controlled nutrient release and soil stabilization, biopolymers can offer positive long-term effects on vegetation growth. Many studies have found a positive relationship between biopolymers and plant growth. In this regard, Niekraszewicz et al. [187] investigated the effect of different biopolymer compositions on the stimulation of plant growth. The authors were able to show that biopolymers-based formulations (chitosan and hemicellulose) have an antiviral action. This action reflects two phenomena: (1) blocking of virus-specific receptors as a result of the affinity of the polymers for these receptors (2) induction of the immune system against pathogens. They showed that the various formulations had a markedly positive impact as growth regulators of germination (accelerating seed germination), growth, and health of the seedlings. In the same context, Kumaraswamy et al. [188] reported that nanocomposites based on chitosan can either be used as biostimulants or biopesticides to fight against diseases and to promote growth. On the other hand, Shamshina et al. [189] reported that adding chitin and its derivatives to the soil promotes the activities of many beneficial microorganisms (chitinolytic microbes), which act as a biological control against many agents responsible for plant infections and diseases. In this regard, Sharp [190] reported that the efficiency of a treatment based on chitin was comparable to those obtained with currently available synthetic pesticides and fertilizers. According to Sharp, this behavior can be explained by the fact that chitin and its derivatives are toxic to pests and plant pathogens as they induce plant defenses and they simulate the activity of beneficial microbes. Similar results have been observed for biodegradable hydrogels based on cellulose, with significantly enhanced plant growth and limitation of the effects of water stress [181]. The effect of vegetal biopolymer as a biostimulant on root growth and resistance to plant stress was recently investigated [191]. The findings of this study demonstrated that vegetal biopolymer-based biostimulants promoted plant growth and significantly protected plants from both abiotic and biotic stress factors.

Few papers to date have investigated the effect of the combination of CRF@BBs on plant growth. Qian et al. [192] compared the effect of conventional MAP granules and CFRs based on polymer-coated MAP granules on wheat, canola, mustard, flax, yellow pea, and alfalfa. Field experiments were conducted in a P-deficient brown soil from Canada. The results showed that the CRFs increased the tolerance of crops to high levels of P placed in seed rows, with levels of 80 kg P_2O_5 ha^{-1} placed in the seed rows. This effect could be explained by the fact that CRFs reduced the salt effect of high levels of fertilizer in close proximity to the seed. Tian et al. [193] investigated the effect of a coated NPK fertilizer without providing details about the nature of the coating. Field experiments were conducted for early ripening rapeseed in the red-yellow soil of southern China. The same amount of non-coated fertilizer (control) and coated fertilizer (CRFs) was applied. The comparison of plant height, first branch numbers, pod numbers, stem dry weight, and pod dry weight between the two treatments revealed that the use of a CRF resulted in a 14.5% higher seed yield than the control. Landis et al. [194] compared polymer-encapsulated sulfur-coated urea to standard fertilizer. The tests were performed on red pine, jack pine, white spruce, and other conifers. The results showed that the seedlings were larger, with fewer culls, when CRFs were used. McKenzie et al. [175] reported that there was no difference between polymer-coated urea and non-coated urea in terms of the grain yield and the grain protein concentration when fertilizers were side-banded in the fall, whereas the use of CRU was highly effective for reducing seedling damage caused by seed row application of urea. A similar finding has also been reported by Middleton et al. [195], who argued that CRU did not injure seedlings even when applied in large quantities. Zhang et al. [176] reported that polymer-controlled-release urea had no effect on the barley grain yield although it did increase its protein content compared to urea.

5. Challenges and perspectives

CRFs show substantial potential in improving nutrients control release and reducing the environmental impact in comparison to traditional minerals fertilizer. Inorganic and/or organic coating materials can be used as diffusion barriers to produce CRF and to control the NPK release rate. However, because of their non-biodegradable and non-renewable character and their potential environmental risks, fossil-based polymers are far from being green and an ideal candidate for coating fertilizers, which limits their commercial application. Hence, biopolymers-based composites and nanocomposites have great potential to be used in environmentally friendly applications such as coating materials for mineral fertilizers.

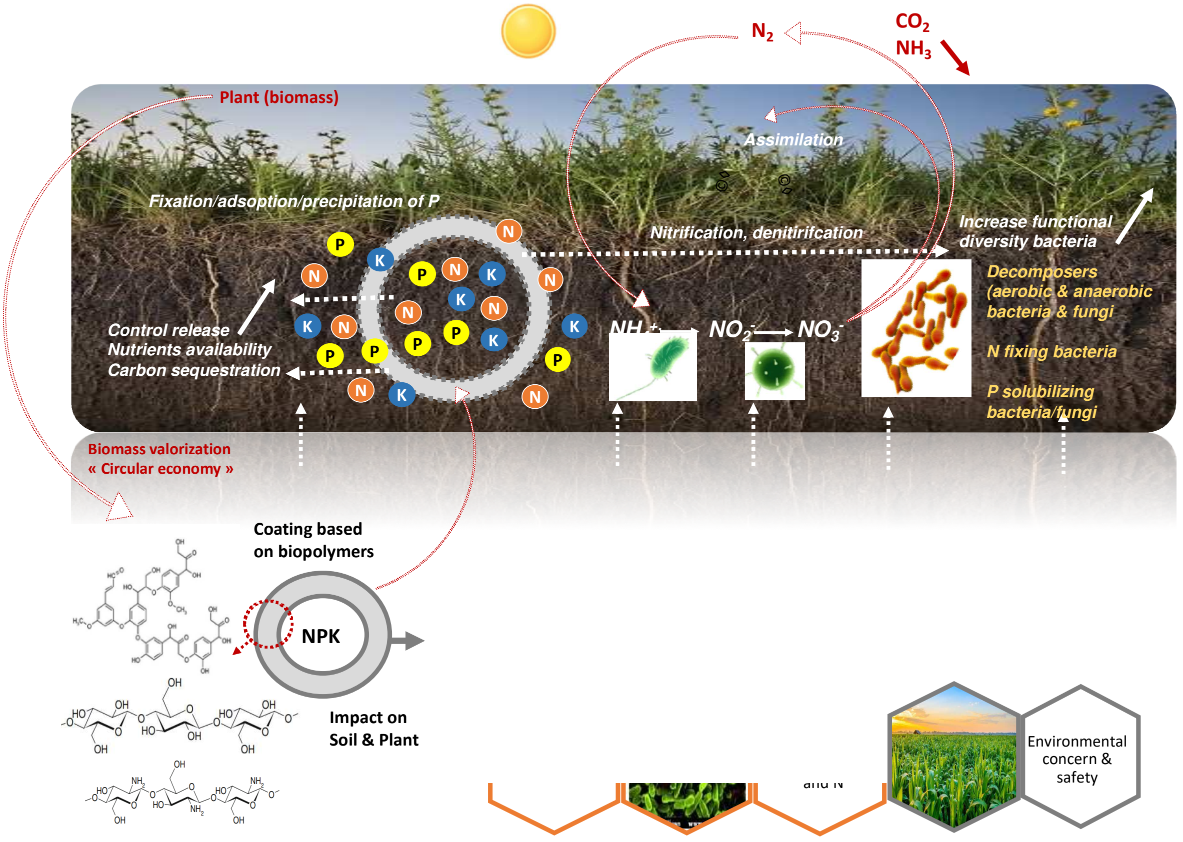


Fig.6. Future perspectives of biopolymers in agricultural application

In response to a strong marketing trend toward more environmentally friendly, organic coating materials based on biopolymers have some advantages and certain important specifications compared to synthetic polymers, which summarized in Fig.6, hydrophilicity and production cost are the most challenges faced by biopolymer-coated fertilizers, and the major limitation that needs to be overcome in order to allow such replacement.

- **Hydrophilicity**: The majority of biopolymers are hydrophilic. To enhance their application in CRFs, several attempts have been investigated to address this challenge and to improve their hydrophobicity by making some chemical modification (i.e. functionalization of molecules [196]). Another option is by adding mineral clay (montmorillonite, kaolin, etc.) [2] or by combining them with other synthetic polymers (polyacrylamide, polyvinyl alcohol, etc.) [197,198].

- **Cost of biopolymers production**: Another several challenge that needs to be overcome to accelerate the commercialization of the final product, is the cost of biopolymer production. The cost depends strongly on the type of biopolymer and production process. In general, biopolymers used for fertilizers coating are extracted from biomass, according to several stages: i) extraction using either a solvent or a chemical catalyst; ii) filtration and washing, iii) purification; iv) drying and lyophilization [94,96]. However, all these additional steps increase the cost of the final biopolymer production, with an additional expense related to adding materials coating on a fertilizer particle (materials coating is expensive compared to uncoated materials as well as the manufacturing process) limit their use on a large scale. Another very important parameter is the availability of biomass (algal, wood, etc.) and the competition or not with other sectors (food/feed, cosmetic). Ideally, in the future, it must be focused on biopolymers, which are not in competition to another fields and their extraction methods do not require high investment cost and do not consume a high quantity of chemical products and high energy, or using waste or co-product biopolymers produced from different biorefinery (Fig.7) (paper industry, oil extraction, sugars fermentation cosmetic extraction).

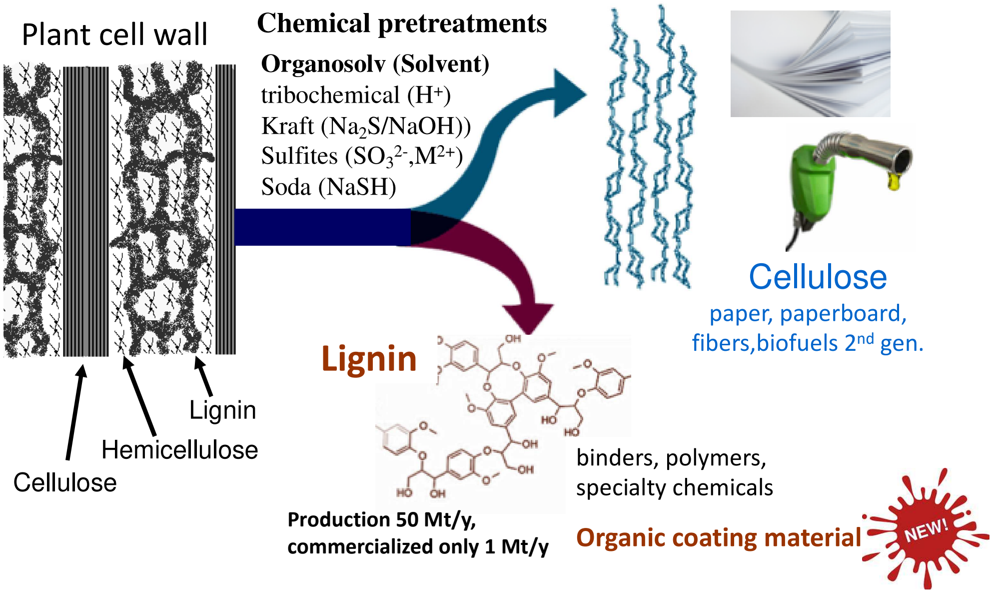


Fig.7. Biorefinery scheme of lignin production as a new organic coating material

There are other several challenges that need to be overcome to accelerate the commercialization of the final product. The relatively constant rate of nutrient elements release under stable temperatures can damage the plant or may not provide the right amount of nutrients at the right time. In fact, plants require different amounts of nutrients depending on their growing stage. When the plant is young, it requires less nutrients than the maturation stage. In addition, the biopolymers used as coating materials are susceptible to biodegradation under particular soil conditions and microorganisms of the ecosystem (susceptible to microbial-enzyme attack), which does not allow the nutrients to be released over an extended period leading.

Another challenge is the use of superabsorbent polymer hydrogels based on biopolymeric materials in improving soil conditions as an environmentally friendly alternative to alkyl acrylate or alkyl methacrylate polymers frequently used as a soil conditioner. To improve the swelling capacity of these biopolymers, to diminish the environmental concerns and waste accumulation caused by non-biodegradable materials and to expand the opportunity to enhance their application in agriculture, several attempts have been investigated. One option is making composites either by adding mineral nanofillers (nanoclay) or by developing composite hydrogels and in terms of structure and architecture of polymer, by making biodegradable amphiphilic block copolymers; because they have the ability to self-associate to form structures of nanometric sizes and varied morphologies. Although the necessity to combine the swelling capacity or water retention with controlled release properties of coating materials still remains a challenge, but the new research strategies based on the principles of green chemistry and the use of biodegradable polymers as new materials with an excellent ability to manage nutrient release profiles; can lead to new discoveries in this field and make these polymers as promoting materials for improved agricultural management.

In view of above mentioned previous studies and challenges, biopolymers are proving to be an ideal candidate to replacing polymers derived from petroleum resources for CRF production. In order to continue to benefit from their particular properties and potential responding to environmental concerns, it would therefore be necessary to develop new organic coating based on biopolymers, more reliable, renewable, not competitive with another industry, less expensive and non-polluting chemical modifications. Due to its functional properties, low cost, and wide sources, lignin has a good potential for preparing controlled-release fertilizers [199]. Lignin (Fig.7) is a phenolic polymer, and one of the main components of lignocellulosic biomass, makes up 15% to 40% of dry matter of woody and gramineous plants. The worldwide production of lignin is estimated to 100 million tonnes/year equivalent to USD 732.7 million in 2015 with only 1-2Mt/year are valorized [200]. Different categories of lignin are produced (ligno-sulphonate, kraft lignins, organosolv) according to classical processes (Kraft process, Sulphite process, Soda process, etc.) that are largely used in the paper industry. Lignin serves also as a cheaper and biodegradable chelating agent to decrease the leaching of iron and zinc [201]. At the same time, lignin, as a urease inhibitor, can reduce the nitrification rate of urea and enable urea to remain in the soil longer [202]. Lignin reduces significantly the release rate of nutrients fertilizer [116,133]. However, lignin presents some disadvantage, for example it is soluble only in alkaline medium, very heterogeneous and with low water retention properties and cannot form a homogeneous film, which decrease its adhesion to NPK surface compared to alginate and chitosan for example. To improve coating properties, lignin also has been modified by physical and chemical methods, for example, steam explosion [203], ammoxidation [204], Mannich reaction [205], phenolation [206], and hydroxymethylation [207]. The mixture of lignin polymer with different organic and inorganic materials (clay, SiO_2, chitosan, nanocelluloses) could improve its cross-link reactivity and to increase its adhesion to mineral fertilizers (NPK). Another strategy is the fabrication of biomimetic superhydrophobic films based on lignin and/or other biopolymers lignocellulosic inspired by plant cell wall and the micronanoscale structural properties of natural superhydrophobic surfaces, such as self-healing, self-cleaning and water/oil separation.

6. Conclusion

Synchronizing nutrient release rate of coated fertilizers with the nutrient demand of plants according to their growth period is one of the most effective and promoting strategy to improve the use efficiency of nutrients and reduce environmental pollution caused by conventional fertilizers. Comprehensive efforts are also being made to strategies that are more efficient to achieve these objectives. Today, biopolymers appear as environmentally green and indispensable materials for replacing oil-based polymers to encapsulate agrochemicals compounds and for various agricultural applications in order to overcome the undesirable environmental impacts and potential contamination ecosystems. These materials should not only fulfil the demands of the market including environmentally, technically, socially and economically sustainable, but also goes a long way toward satisfying future requirements to produce smart polymers with biodegradable and renewable properties in nanotechnology concept. In addition, study the different environmental conditions that may influence these biofertilizers based on biopolymers efficiency, such as temperature, soil type, moisture, etc.

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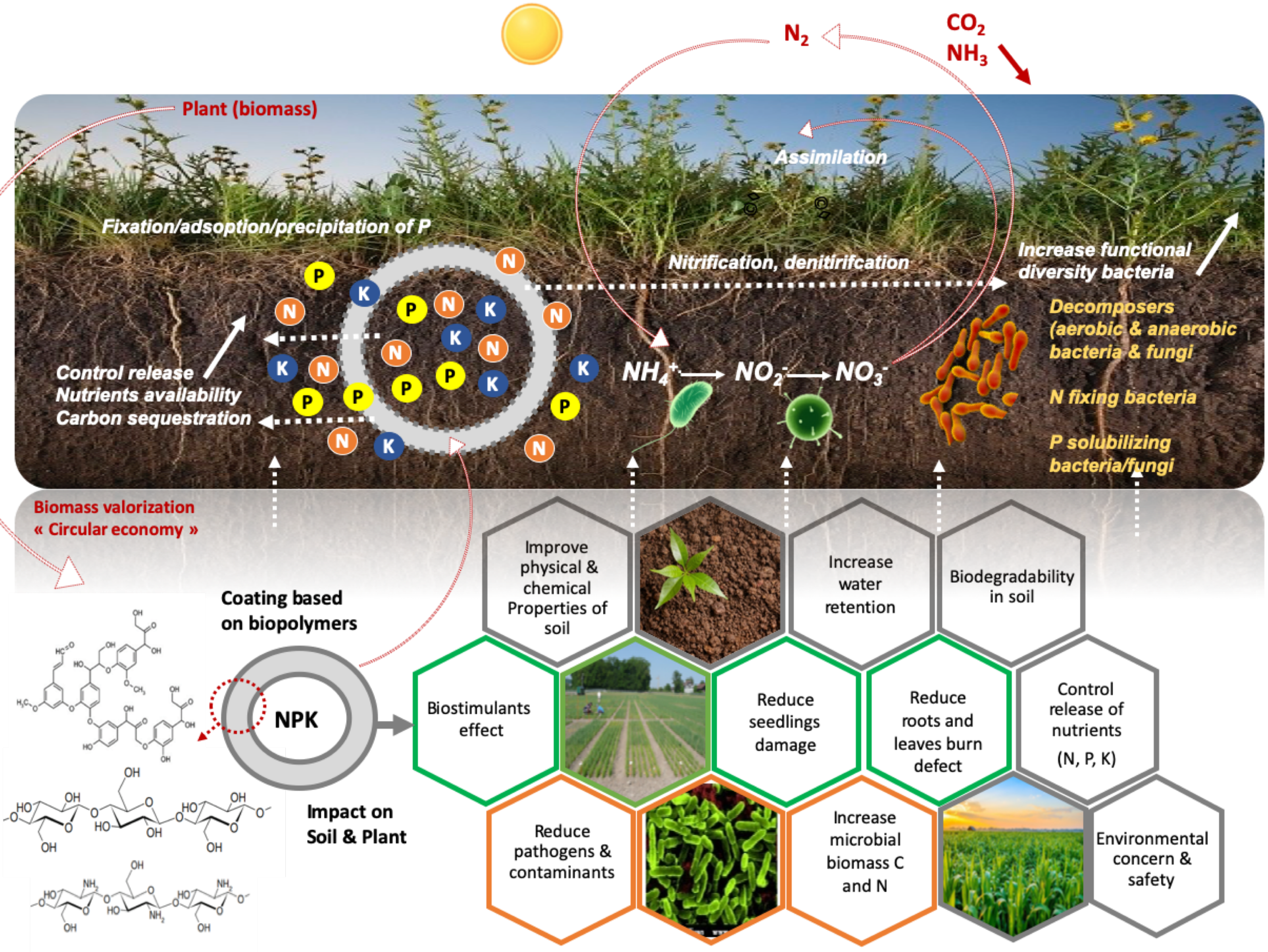
N_2
CO_2
NH_3
Plant (biomass)
Assimilation
Fixation/adsoption/precipitation of P
Nitrification, denitirifcation
Increase functional diversity bacteria
Decomposers (aerobic & anaerobic bacteria & fungi
N fixing bacteria
P solubilizing bacteria/fungi
Control release
Nutrients availability
Carbon sequestration
$NH_4^+ \longrightarrow NO_2^- \longrightarrow NO_3^-$
N
P
K
Biomass valorization
« Circular economy »
Coating based on biopolymers
NPK
Impact on Soil & Plant
Improve physical & chemical Properties of soil
Increase water retention
Biodegradability in soil
Biostimulants effect
Reduce seedlings damage
Reduce roots and leaves burn defect
Control release of nutrients (N, P, K)
Reduce pathogens & contaminants
Increase microbial biomass C and N
Environmental concern & safety