Conception of phosphorus fertilizers based on biopolymers Impact on soil properties

Saloua Fertahi

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Conception des engrais phosphatés à base de biopolymères : Impact sur les propriétés d'un sol

Présentée par Saloua FERTAHI
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Sous la direction de Madame Isabelle BERTRAND
et Monsieur M'barek AMJOUD

Devant le jury composé de

Mustapha RAIHANE, professeur d'enseignement supérieur, FST Marrakech	Président
Johnny BEAUGRAND, directeur de recherche, INRAE Nantes	Rapporteur
Khalid DRAOUI, professeur d'enseignement supérieur, FS Tétouan	Rapporteur
Christian MOREL, ingénieur de recherche, INRAE Bordeaux	Examinateur
Hanane HAMDALI, Professeur habilité, FST Béni Mellal	Examinatrice
Isabelle BERTRAND, directrice de recherche, INRAE Montpellier	Directrice de thèse
M'barek AMJOUD, professeur d'enseignement supérieur, FST Marrakech	Co-directeur de thèse
Abdellatif BARAKAT, directeur de recherche, INRAE Montpellier	Co-encadrant
Abdallah OUKARROUM, enseignant chercheur, UM6P Benguerir	Invité
Youssef ZEROUAL, Chercheur, OCP group	Invité

UNIVERSITÉ DE MONTPELLIER

Montpellier SupAgro

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Encadrants :

- **Isabelle BERTRAND**, directrice de recherche, unité mixte de recherche Ecologie fonctionnelle et biochimie des sols (Eco&Sols), INRAE Montpellier
- **M'barek AMJOUD**, professeur de l'enseignement supérieur, Matériaux Innovants, Énergie et Développement Durable (IMED-lab), Faculté des Sciences et Techniques-Marrakech, Université Cadi Ayyad
- **Abdellatif BARAKAT**, directeur de recherche, unité mixte de recherche Ingénierie des agropolymères et technologies emmergeantes (IATE), INRAE Montpellier et AgroBioSciences, UM6P

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الحمد لله الذي بنعمته تتم الصالحات، وبفضله تتنزل الخيرات والبركات، وبتوفيقه تتحقق المقاصد والغايات

RÉUMÉ

La majeure partie du phosphore (P) utilisé dans les engrais provient de roches phosphatées, une ressource naturelle rare qui doit être préservée. Une option consiste en une meilleure optimisation de l'efficience d'utilisation du P par les plantes. Depuis plusieurs années, des engrais phosphatés à libération contrôlée ont été développés avec des enrobants formulés à base de polymères pour réduire les interactions entre le P et les minéraux du sol, et augmenter la synergie entre la libération de P et les besoins des plantes. Toutefois, leur coût de production reste un frein majeur pour leur utilisation. De plus, la majorité des polymères utilisés ne sont pas dégradables dans le sol. L'objectif de ma thèse est (1) d'utiliser des biopolymères issus de déchets de biomasse végétale pour préparer des formulations d'enrobage (2) de tester ces enrobages sur des granules de triple superphosphate (TSP), de les caractériser et d'étudier leur dissolution dans l'eau, (3) d'évaluer leur effet sur les propriétés d'un sol méditerranéen de grande culture. Les différents engrais enrobés formulés à base de lignine extraite de grignons d'olive, de polysaccharides (carraghénane, carboxymethyl de sodium, d'alginate de sodium), et de plastifiants (polyéthylène glycol, glycérol) ont montré une libération plus lente du P dans l'eau, comparé aux engrais non enrobés. La vitesse de libération du P dépend de l'épaisseur de l'enrobant, de son élasticité, de son allongement, de son hydrophobicité et de son hygroscopie. Sur l'ensemble des formulations testées, les engrais enrobés à base de lignine et de lignine-carraghénane présentent la vitesse de libération du P la plus lente. Une attention particulière a été accordée à ces deux formulations pour étudier leur effet sur les propriétés d'un sol. Ces engrais enrobés, lors de leur dissolution dans un sol, acidifient légèrement le sol et présentent une distance de migration du P de 14 mm de diamètre. Les engrais non enrobés acidifient davantage le sol et présentent une zone de migration du P plus étendu (21 mm de diamètre) et ce après une même durée de 28 jours. Cependant, après 28 jours, l'enrobage des TSP n'a pas impacté la disponibilité du P dans le sol. Cependant, les engrais enrobés tendent à augmenter la concentration en P microbien du sol.

ABSTRACT

Most of the phosphorus (P) used in fertilizers comes from phosphate rocks, a rare natural resource that must be preserved. One option is to better optimize the efficiency of P use by plants. For several years, controlled release phosphate fertilizers have been developed with polymers-based coatings to reduce the interactions between P and soil minerals and increase the synergy between P release and plant needs. However, their production cost remains a major obstacle to their use. Moreover, most of the polymers used are not degradable in the soil. The objective of my thesis is (1) to use biopolymers derived from vegetal biomass waste to prepare coating formulations (2) to test these coatings on triple superphosphate (TSP) granules, to characterize them and to study their dissolution in water, (3) to evaluate their effect on the properties of a Mediterranean field crop soil. The different coated fertilizers formulated based on lignin extracted from olive pomace, polysaccharides (carrageenan, sodium carboxymethyl, sodium alginate), and plasticizers (polyethylene glycol, glycerol) showed a slower release of P in water, compared to uncoated fertilizers. The rate of P release depends on the thickness of the coating, its elasticity, its elongation, its hydrophobicity and its hygroscopy. Of all the formulations tested, coated fertilizers based on lignin and lignin-carrageenan had the slowest P release rate. Special attention was paid to these two formulations to study their effect on soil properties. These coated fertilizers, when dissolved in soil, slightly acidify the soil and have a P migration distance of 14 mm in diameter. Uncoated fertilizers further acidify the soil and have a larger P migration zone (21 mm in diameter) after the same 28-day period. However, after 28 days, the TSP coating did not affect the availability of P in the soil. However, coated fertilizers tend to increase the microbial P concentration in the soil.

ABBREVIATIONS

F	Fertilizer
CRF	Controlled release fertilizer
SRF	Slow release fertilizer
BCF	Biopolymer coated fertilizers
TSP	Triple superphosphate
OP	Olive pomace
LG	Lignin
AG	Sodium alginate
CM	Sodium carboxymethyl cellulose
CR	K-carrageenan
PEG	Polyethylene glycol
LGAG	Lignin-alginate
LGCM	Lignin-carboxymethyl cellulose
LGCR	Lignin-carrageenan
LGCR-GL	Lignin-carrageenan-glycerol
LGCR-P200	Lignin-carrageenan-PEG 200
LGCR-P2000	Lignin-carrageenan-PEG 2000
TGA	Thermogravimetric analysis
FTIR	Fourier-transform infrared spectroscopy
SEM	Scanning electron microscopy
HPLC	High-performance liquid chromatography
EB	Elongation at break
EM	Elastic modulus
TS	Tensile strength
CA	Contact angle
IS	Ionic strength
EC	Electric conductivity
AER	Anion exchange resin

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GENERAL INTRODUCTION

Today, more than 80% of phosphate rocks are dedicated for fertilizer industry [1] whereas phosphorus (P) resources are in exhaustion phase. Only 0.12% of earth crust is made up of P mineral. The phosphorus reserves are spread unequally in the world. Only few countries have significant stocks. The largest remaining fossil phosphorus resources are mainly located in Morocco, China, South Africa, United States and Jordan [2]. The exploitation of phosphorus impoverishes the current stocks [1,3]. However, fossil phosphate resources have accumulated over many millions of years [4] and are considered as non-renewable resource [5]. In a world population that projected to reach nine billion in 2050, producing enough food is likely to be a substantial challenge for humanity. The world phosphate fertilizer demand continues to run. It is expected to reach 45.858.000 tons (P_2O_5) in 2020, while it was 41.151.000 tons in 2015 [6]. With the depletion of phosphorus, food availability and security will eventually be threatened. In addition, phosphorus scarcity could induce to geopolitical implication, as phosphorus reserves are found in a limited number of countries.

In the other hand, the world waste generation is predicted to reach 3.4 billion tons in the coming 30 years, representing an increase of 70% in global waste by 2050 [7]. Recycling existing materials and products as long as possible is a good way to reduce waste to a minimum. The concept of circular economy appears to encourage recycling of products reaching the end of their life. Their materials are kept within the economy wherever possible and can be productively used repeatedly, thereby creating further value.

Phosphorus deficiency in worldwide soils is widespread, with 43% of the world's soils being deficient in phosphorus [8]. Phosphorus is often the most limiting plant nutrient [9]. Sometimes, the phosphorus deficiency is not because the amount of total phosphorus in soil is low but rather because the phosphorus in soils is in chemical forms that are not available to plants [9,10]. The phosphorus fertilizers are applied to soils to increase the bio-available supply of orthophosphate to the roots. However, due to the low efficiency of soil phosphorus fertilizers, only 10-20% of phosphorus is taken up by the plant [11–13]. The non-absorbed part of phosphorus is adsorbed by the solid phase in soils and onto surface of clay-sized minerals dominated by aluminum and iron oxides [14], or precipitated as Ca-phosphates in highly calcareous soils [10].

The currently available forms of phosphorus fertilizers require further improvements to increase their efficiency in soils. Recently, “controlled release fertilizer” (CRF) has been developed for this reason [15]. CRFs are designed fertilizers that release nutrients in a controlled delayed manner matched with the sequential needs of plants. Several studies have shown the high efficiency of phosphorus CRFs compared to conventional fertilizers [8,16]. Coating with an insoluble material is one of the methods commonly used for CRF formulations. Biopolymers

are considered potential and attractive candidates for mineral fertilizer coating [17–20]. In most coating formulations; plasticizers are added to improve the flexibility, tensile strength, and adhesion properties of polymeric membranes [21,22].

Although the literature agrees on the beneficial influence of biopolymer-based coatings, the effect of the origin and the nature as well as the structure of biopolymers are rarely taken into account. We also lack information on the possibility of using biopolymers derived from biomass and organic waste as efficient coatings. In this context, the first objective of the present thesis is to study whether the phosphate fertilizers coated with lignin extracted from olive pomace, and other commercial biopolymers from seaweeds or lignocellulosic materials as well as plasticizers are endowed with dissolution and degradation characteristics in soil that could improve their efficiency. Another main objective is to bring new understanding elements on the relationship between the coating agents' properties and the phosphorus release. The first chapter describes the literature review and introduces the main considered approaches, aims and structures of my thesis. In the chapter II, I described the materials and methods used in this thesis. Chapter III investigates the effect of biopolymers origin and nature as well as plasticizers addition on coatings properties and on phosphorus release in water and Chapter IV investigates the effect of coated phosphorus fertilizer on some chemical and biological soil properties. Finally, an overall conclusion of the work includes major results and proposes some perspectives for further research work.

CHAPTER I. Review of bibliography

In this chapter, a comprehensive literature review on the coated fertilizers based on biopolymers and their effects on some soil properties were presented. First, granular fertilizers commonly used were introduced as well as their properties, then a global description of controlled release fertilizers, their classification and advantages/disadvantages were presented. After that, a special focus was oriented to the coated fertilizers and biopolymers used as coatings, coating methods, nutrients release medium and mechanisms as well as parameters controlling the nutrients release. Finally, the effect of coated fertilizers on soil pH, soil microbial biomass and nutrients bioavailability were presented.

1. Conventional granular fertilizer

There are three types of the main commonly used granular fertilizers, based of one or more primary nutrients (nitrogen N, phosphorus P and potash K): straight fertilizers (N, P or K), binary fertilizers (NP, PK, NK) and ternary fertilizers (NPK). Fertilizer labels have three bold numbers. The first number is the amount of nitrogen (N), the second number is the amount of phosphate (P_2O_5) and the third number is the amount of potash (K_2O) (Fertilizer grade: (% N, % P_2O_5, % K_2O)).

The main straight granular fertilizers commonly used are urea (46, 0, 0), simple superphosphate SSP (0-16-0) and triple superphosphate TSP (0-46-0). Urea is produced from ammonia and carbon dioxide and has the highest nitrogen content. SSP and TSP are manufactured by acidulation of phosphate rocks with sulfuric (for SSP) or phosphoric acids (for TSP). The chemical description is given in **Equation 1** [23]. Degree of acidulation is a function of x and y. For SSP, y = 1, x = 0 and for TSP, y = 1, x = 6

$$Ca_{10}(PO_4)_6F_2+y(6-x)H_2SO_4+2xyH_3PO_4 \rightarrow y(6-x)CaSO_4+(3+x)yCa(H_2PO_4)_2,H_2O+(1-y)Ca_{10}(PO_4)_6F_2 + yCaF_2 \quad \textbf{Equation 1}$$

For binary fertilizers, monoammonium phosphates MAP (11-52-0) and diammonium phosphates DAP (18-46-00) are commonly used and are manufactured by ammoniation of phosphoric acid (**Equation 2**) [23]:

$$NH_{3(g)} + H_3PO_4 \rightarrow NH_4H_2PO_4 \xrightarrow{NH_3} (NH_4)_2HPO_4 \qquad \textbf{Equation 2}$$

The ternary NPK fertilizers are generally used with different compositions, and are produced by two processing methods; either by granulate NPK powdery fertilizer materials into granules

or to blend different ready-made N-fertilizer pellets, P-fertilizer pellets and K-fertilizer pellets (fertilizers mixture). **Table I-1** presents granular fertilizers commonly used and their characteristics [24,25]**.**

Table I-1: Granular fertilizer commonly used and their characteristics

Main used granular fertilizer		Size (mm)	Formulation	Color	Composition		
					N %	P_2O_5 %	K_2O %
Single superphosphate	SSP	-		Gray	0	16	0
Triple superphosphate	TSP	1-4	$Ca(H_2PO_4)_2$	Beige gray	0	46	0
Diammonium phosphates	DAP	1-4	$(NH_4)_2HPO_4$	Greenish	18	46	0
Monoammonium phosphates	MAP	1-4	$NH_4H_2PO_4$	Whitish	11	52	0
NPK	NPK		-	Different color	-	-	-
Urea		1-2	$(NH_2)_2CO$	white	46	0	0

2. Background about controlled release fertilizers

2.1. Terminology: controlled and slow release fertilizers CRFs vs SRFs and legislations

Release and slow release fertilizers are defined by the European Standardization Committee as follow [26]:

- 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 the European Standardization Committee, a fertilizer may be described as slow-release if the nutrient or nutrients achieve three criteria in soil, under defined conditions – including at a temperature of 25°C [18,26,27]:

1) No more than 15% (w/w) of the weight of the fertilizers, released in 24 hrs;

2) No more than 75% (w/w) released in 28 days;

3) At least 75% (w/w) released at stated release time.

2.2. Classification of CRFs

CRFs/SRFs can be generally classified into three major categories [28–32], outlined in the **Figure I-1:**

- **Organic substances**: They are divided to synthetic organic-N low-solubility and natural compounds. The former can be divided into biologically decomposing compounds 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 phosphates rock (PAPR).
- **Water soluble fertilizers with physical barriers**: These barriers can be done either by coating cores or granules with sulfur/polymer materials, or incorporating nutrients into matrices that restricts the dissolution of the fertilizer. The coated fertilizers can be further divided into fertilizers coated with organic polymer that are either thermoplastic or resins, fertilizers coated with inorganic materials such as sulfur-or mineral-based coatings, and fertilizers coated with mixture of sulfur and organic polymers. The matrices can be produced by hydrophobic materials such as polyolefines, rubber, etc., and gel-forming polymers (hydrogels). Coating using sulfur was used in the past while it is rare now because of its low wettability and adhesion to the coated core [33,34]. Matrices based on hydrophobic materials or gel-forming polymers are used but less common compared to coated CRFs. The most used category is granules/cores fertilizers coated with organic polymer materials [28–32].

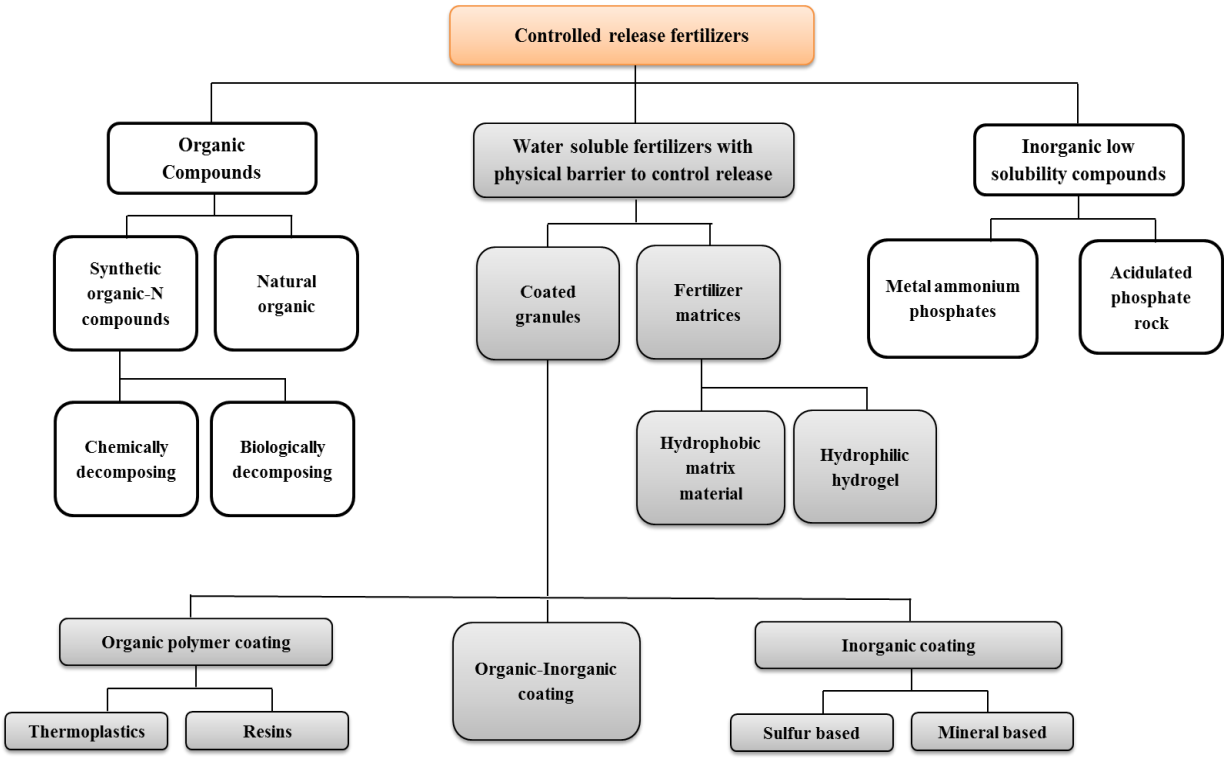


Figure I-1: Classification of controlled release fertilizers (CRFs) [32]

"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 coated fertilizers, 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 [35]. 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".

2.3.Efficiency of CRFs compared to traditional fertilizers

In this paragraph, we will see in details the major problems related to conventional fertilizers and solutions provided by CRFs as well as the inconveniences generated.

Supply of nutrients is often inconsistent with the plant need. The plant consumes only a part of chemical fertilizers and the rest is lost in the environment [36], which decrease their efficiency. About 40–70% of nitrogen are lost through leaching, mineralization, NH_3 volatilization, gas emissions (nitrous oxide NOx), soil erosion and denitrification processes. 80–90% of phosphorus are lost due to surface run-off and mineralization (fixation of P and formation of Fe- and Al-based oxides), and 50–70% of potassium are mainly lost by leaching associated to water movement in the soil and surface run-off [18]. This potential nutrients loss causes not only economic damages, but also environmental issues. Nitrates from nitrogen fertilizers contaminate the groundwater by leaching and accumulation from agricultural activities, which deteriorate drinking water quality. The NH_3 volatilization also pollutes the air and provokes adverse atmospheric effects and hazardous emissions. The phosphorus overflow generates the eutrophication phenomenon in fresh water and estuaries; which overstimulates the growth of algae blooms and contributes to a wide range of water-related problems. Excessive fertilizer use could negatively affects soil quality through acidification, persistent organic pollutants and heavy metal accumulation [37].

CRFs show improvement in the efficiency of fertilizers while decreasing the negative effects related to conventional fertilizers. CRFs liberate slowly the nutrients to insure synchronization with crop requirement. In fact, the plant takes advantage from the fertilizer without osmotic stress or roots and leaves burn defect caused by high concentration of soluble salts from conventional fertilizers. CRFs may increase the nutrients availability and produce greater yields. The effect of CRFs on soil and plant will be detailed in the section 4 of this chapter**.** CRFs can also generate savings in the fertilizer quantity by reducing nutrient losses. A decrease of 20 to 30% of the recommended application rate of a conventional fertilizer is possible when applying CRFs while maintaining the same yield [26]. Savings can also occurred in the labor, time and energy. In fact, CRFs can meet the crop nutrient demand for the entire season through a single application, reducing the frequency of application and involving savings in spreading costs. Despite these advantages, the manufacturing cost of most coated or encapsulated CRFs is still considerably greater than that of conventional mineral fertilizers due to the price of materials and process. Another major problem of CRFs is that some 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/year and 500 kg/ha need almost ten years to be decomposed to only 200 ppm of dry soil [11,26,30,32,38].

3. Biopolymer coated fertilizers (BCF)”

In this manuscript, we will present the polymeric materials used as coatings, with a focus on biopolymers. We will name it “Biopolymer coated fertilizers (BCF)”.

3.1.Biopolymers widely used for BCF production

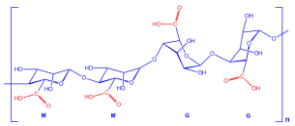
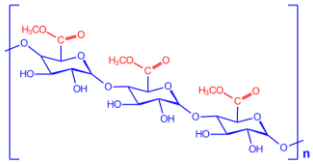
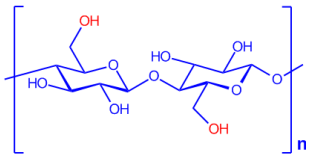
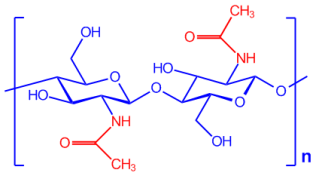
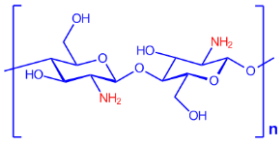
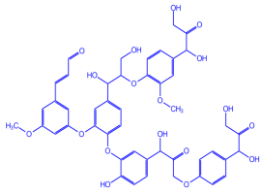
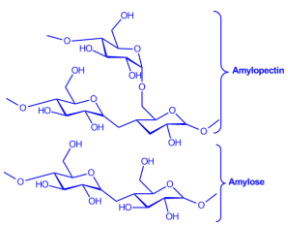
There is a debate to define a biopolymer; some researchers define it as a polymer derived from biomass, produced by living beings (plants, algal, animals, fungi, etc.). Others say that every biodegradable, biocompatible and nontoxic polymer can be considered as a biopolymer, even if it is synthetic, i.e. poly (lactic acid) PLA [39,40], polyvinyl alcohol PVA [19,41], poly (butylene succinate) PBS [42], Polydopamine [43,44]. Along this manuscript, we will use the term ‘biopolymers’ for polymers derived from renewable natural resources, i.e. starch [41], lignin [16,45], cellulose [12,21,46–49], chitosan [17–20], carrageenan [50], guar gum [51], xanthan gum [22], natural rubber [39], etc.

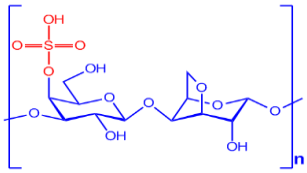
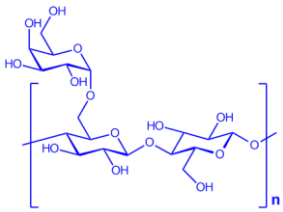
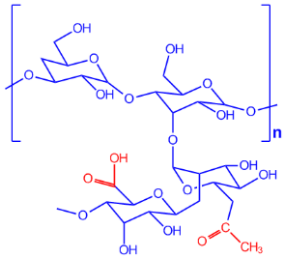
Biopolymers are known for their price relatively cheaper than conventional coating materials (thermoplastic resin and thermosetting resin) [52], their higher biodegradability, less toxicity to the soils as well as hydrogel forming properties that improve soil water-holding capacity

[53,54]. In addition, biopolymers can be used as a soil amendment [55] and a stimulating of the dormant microbial activity [56]. These characteristics make them promising candidates for coating. The most used biopolymers, their origins and their extraction methods are cited in the **Table I-2**.

Despite these properties, some inherent characteristics of biopolymers (such as hydrophilicity, poor mechanical properties, etc.) need to be improved [32,55]. Modifications or the addition of other materials (i.e. plasticizers) to biopolymers formulations have generally performed to make them more convenient for coating. For instance, chitin is modified by deacetylation to convert it to chitosan [57] that presents remarkable properties of film formation. The incorporation of crosslinkers [58–60], compatibilizers [49] and plasticizers [21,22,61,62] on the coating solutions has also reported to be a good option to enhance flexibility, tensile strength and adhesion properties of polymeric membranes [21,22]. Blending and copolymerization of different biopolymers between them or with synthetic polymers have also caught interests and they have been the subject of several works. Researchers have tested various possibilities: natural rubber and starch [63], lignin and ethylcellulose [64], starch with lignin [65], starch and polyvinyl alcohol (PVA) [41,61], starch-g-poly L-lactide (PLLA) [66] , sodium alginate-g-poly (acrylic acid-co acrylamide) [67], sodium alginate-g-poly (acrylic acid-co acrylamide) [36,68], carboxymethyl chitosan (CMCS)-g-poly (acrylic acid) [69], guar gum-g-poly (itaconic acid-co-acrylamide) [51], starch-g-poly (vinyl acetate) [66], starch-g-poly (acrylic acid) [70], sodium carboxymethylcellulose (CMC)-g-hydroxyethylcellulose (HEC) [71]. These works show the effectiveness of these combinations as coating agents to slow down the release of nutrients through the coated fertilizers.

Table I-2: Most used biopolymers as coatings, their structure, origins and some extraction methods

Biopolymer	structure	Origins	Extraction methods
Alginate		-Brown algae	-The seaweeds powders were treated many times with (2% aqueous solution of $CaCl_2$, HCl 0.01M, pH 2, during 3 hours at 70°C with mechanical stirring), centrifuged, solubilized in Na_2CO_3 (3%) and recovered after dialysis [72]
Pectin		-Primary cell walls and the middle lamella of higher plants (citrus peel, apple pomace, sugar beet pulp [73]	- Boiling aqueous solution of HNO_3 at different conditions in a heating mantle under a reflux system. After centrifugation (4695.6 ×g, 20 min, 4 °C), the supernatant was filtered and precipitated with absolute ethanol 1:2 (v/v) [74]
Cellulose		-Crop plants, wood, cotton, algae, biomass wastes [75]	- Dispersion of dry powder in water at 2% (w/v). After centrifugation (2500rpm, 30min), a sodium hydroxide solution 4wt% was added to the resultant pellet (80°C, 2h and 150 rpm). This treatment was repeated, and the sample was washed thoroughly with water, centrifuged and dried at room temperature [75]
Chitin		-Invertebrates (Crustacean shells, insect cuticles…), fungi, green algae, cell walls and yeasts [76]	-Chemical extraction include 3 steps: *Deprotonation (0.125 to 5M, NaOH, at varying temperature and treatment duration. *Demineralization (0.55-1.5M, HCl, 35-50°C, 30min-6h) * Discoloration (organic solvent mixture or acetone to eliminate pigments) [77]
Chitosan			-Deacetylation of chitin (concentrated NaOH solution for few hours) [77]
Lignin		-Lignocellulosic materials (agricultural residues, wood [78]	-Fractionation process (ternary mixture solvent (methyl isobutyl ketone, ethanol and water (25,42, 33% v/v) in presence of H2SO4 0.025 M. The reaction was performed at different temperatures (140, 160, 180°C), 40min, N2(20bars) and 100 rpm. The reaction was stopped by quenching on ice (10min), the mixture filtered, and the solid fraction was washed by distilled water (neutralization to pH 6-7) [78]
Starch		-Maize, Wheat, Rice, Cassava [79]	-H_2SO_4 (0.15% w/w, 16h at room temperature) followed by centrifugation (5000 r/min, 10min), washed with anhydrous ethanol and acetone and dried at 40°C [80]

Carrageenan		-Red algae	-Seaweed was mixed with KOH (6% w/v), and the reaction was carried out at 80°C for 3h. Then, the slurry was filtered, and the carrageenans in the permeate were precipitated in 80% isopropanol, filtrated and recovered by freeze-drying [81]
Guar gum		-Seeds	-Crushed seeds were immersed in NaCl solution (5%, pre-adjusted to pH 3 with acetic acid) for 24h at 50°C and 300rpm. The mixture was sieved, treated with (90% ethanol and 10% isopropanol), centrifuged (6000rpm, 7min). Then the obtained gum was dissolved in clean water, precipitated in (90% ethanol and 10% isopropanol), filtrated and dried at 50°C [82]
Xanthan gum		-Xanthomonas bacteria	-Fermentation of glucose by various species of Xanthomonas bacteria [83]

3.2.Release mediums

The nutrients release behavior and rate are the most important properties for CRFs. To test the release rate of nutrients from coated fertilizer, authors used generally water [40,59,66,67,70,84], soil [22,58,85] or both systems [66,86] and a minority used saline solutions [87,88]. Most researchers choose distilled water to measure the rate of release, as it is easiest and less variable than soil tests, which are related to soil properties. As expected, the release behavior in water is not similar to that in soil. Niu et al. [89] claimed that coated urea released 5, 8, and 52% of nitrogen within 2, 5, 30 days respectively in soil, whereas the release rate of nitrogen in water is very fast (98% in 2 days). Perez-Garcia et al. [21] and Zhang et al. [68] confirmed this result. According to Zhang, the release rate of nitrogen through the coated fertilizer was lower in soil than in water; about 40 and 90% was released in soil after 2 and 8 days respectively, while in water, approximately 56% and 90% was released within 1 and 3 hours, respectively. However, few authors such as Jia et al. [44] reported that the rate of P and K released through coated fertilizer in soil was slower than in water, whereas it was opposite for N .

3.3. Mechanisms through coated fertilizers

Several research have been reported to identify and understand the controlled release mechanism from coated fertilizers and its different stages. It is not easy to define the release mechanism because it depends on many factors; coating materials composition, porosity, thickness, solubility of coating materials and core materials, soil properties (type, temperature, water content, environmental pH, microbial activities, etc.). In this section, we will not discuss the behavior and interactions of coated fertilizer and soil, but we will focus only on the release mechanisms of nutrients through the polymeric coating materials when coated fertilizers get in touch with water (in the case of release test in water) and with soil solution. Morgan [90] argued that the most polymer-coated products release nutrients is by diffusion through a semi-impermeable membrane. Shaviv [27] and Liu [91] developed a famous model named: "multi-stage diffusion model", in water. According to this model, the coated fertilizer needs to get in touch with water, to liberate nutrients. In the first stage of the release process, the water penetrates through the coating membrane and it condenses on the solid core followed by partial nutrient dissolution. Due to this dissolution, an internal pressure (or osmotic pressure) builds within the granule and it swells. Two phenomena may take place in 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 diffusion mechanism and has been managed by the concentration gradient across the coating, or by the pressure gradient, or by both forces. Whereas, if the internal pressure surpasses the membrane resistance, the "failure mechanism" or "catastrophic release" occurred; it is the entire content release due to the rupture of the coating material and then the bursting of the granule (**Figure I-2**). The catastrophic release usually produces by frail and non-elastic coating such as sulfur based coating. Besides, biopolymer-coated fertilizers are known by their slow release mechanism. Interactions between the fertilizer granule and the polymer layer are physical rather than chemical [42]. Wu et al. [18] proposed a release mechanisms model of nutrients in soil from polymeric coated fertilizers, especially from double coated fertilizer with superabsorbent as outer coating. The first step is that the layer is slowly swollen by the soil solution and transforms to hydrogel. A dynamic exchange between the free water in the hydrogel and the water in soil will occur. After that, the free water in superabsorbent layer will migrate to the middle layer, and water will penetrate slowly through the inner coating in the initial stage and compounds in the fertilizer will dissolve. In this stage, diffusion would be the release rate-limiting step. Under the effect of water, ions and microorganisms existing in the soil, the middle layer will slowly degrade in the last stage

and continue to dissolve nutrients. In this stage, degradation rate determines the nutrients release rate. Finally, the dissolved compound fertilizer diffuses out the middle layer and enters into the outer layer, and then releases into the soil through the dynamic exchange of free water.

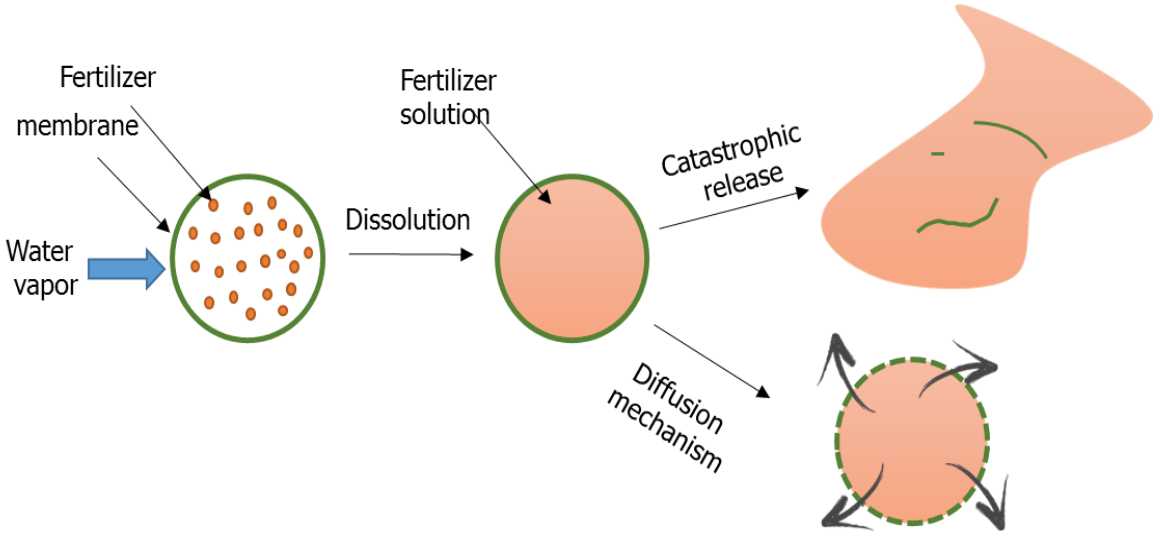


Figure I-2: Release mechanisms of nutrients through polymeric coating, in contact with water (or soil solution) [27,91]

3.4.Coating parameters controlling the nutrients release

Many factors affect the release rate of nutrients through these coatings based on polymers (**Table I-3).** The most important parameters are: polymers nature (hydrophilic or hydrophobic), their concentration in the coating solution, solution viscosity, added modifying agents, number of layers, techniques used in coating, time, etc. All that influence the thickness, the porosity and the morphology of the coating layer [46].These parameters are in interdependencies and govern the nutrients release rate [21,46,47,49,63,84]. We will see in details each parameter.

3.4.1. Coating method

Coating of granular fertilizers (F) can be applied by various methods such as spraying a liquid, dipping into a liquid, precipitating from supercritical fluids, or depositing a powder using an electrostatic technique [92]. The most used techniques for coating fertilizers are: immersion of the fertilizing granule into a polymer solution or spraying this liquid onto the granules (**Figure I-3**). Spraying is commonly carried out either in a coating pan (rotary drum) or a fluid bed coater [93].

Immersion: realizes by dipping the fertilizer into the polymer coating solution [94]. The solution adheres to the granule surface of fertilizers and fixed by a drying system.

Coating pan: is one of the most used techniques to coat fertilizer granules using polymeric solutions. The coating liquid is transferred through the spray to the surface of beads already present in the spray zone. The system is provided with 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 dry coated particles. The coating is realized by two systems; the first one is cascading layer composed of a thin layer of granules that flows down the free surface, and the second one is quasi-static zone comprising of remaining granules that rotates as a fixed bed. As the pan rotates, the beads cascade through the spray zone under gravitational force. Granules come in contact with the spray and get coated with the coating solution followed by drying before moving into the bulk of the tablet bed. After a rotation time, the beads may re-enter to the spray zone and the coating and drying process are repeated. The granule's residence time at the surface of the cascading bed determines the quantity of solution received by a granule per pass through the spray zone. Quality and performance of a coating are influenced by several parameters: simultaneous exchanges of heat and mass between coater pan and inlet air stream, spraying material and substrate, dimensions, rotational speed, configuration and number of baffles, pan loading, bed humidity and pan coater temperature [92,95].

Fluidized bed (Wurster): is used to solid granules coating such as pellets, granules or powders. It's widely used in pharmaceutical industries, food, feed and fertilizers [96]. Fluidized beds are based on the fluidization of the initial granules by hot air, while a suspension or solutions sprayed on them. There are three commonly used configurations of fluidized bed; top spray, bottom spray and side spray. In regards the coating of fertilizers, Wurster fluidized bed, which is a modified bottom spray fluidized bed, is the most suitable apparatus to coat fertilizer. 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 [93,97,98]. The key variables that control this coating process are classified into three aspects; the first one is related to fluidization, which is controlled by the input air flow rate, dimensions and type of the equipment, particle size and density, the substrate surface characteristics and the batch size. The second one is related to coating. It is identified by the position and the design of the nozzle, droplet size, viscosity, surface tension and density, injection pressure, and atomizing air as well as coating liquid flow rate. The third aspect is the drying parameters; including inlet and outlet temperature as well as inlet air flow rate, and air humidity [93,96,99].

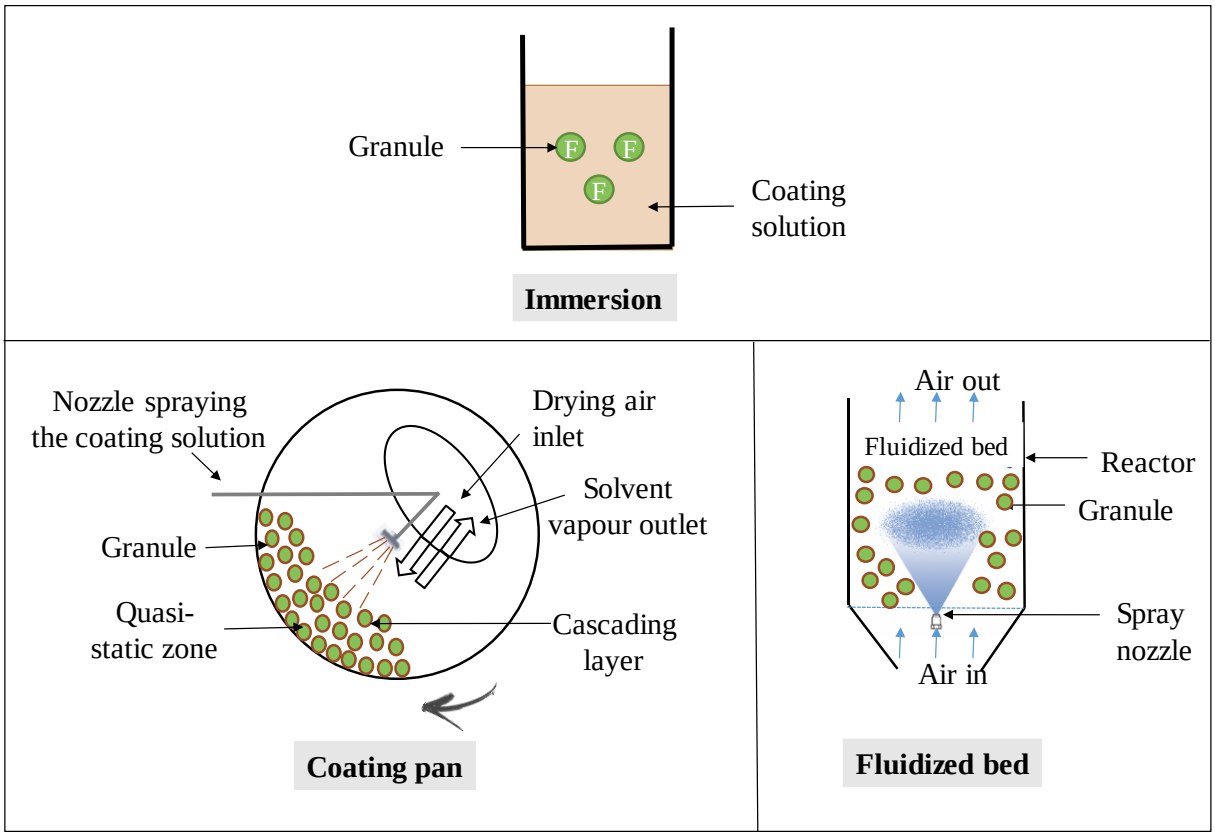


Figure I-3: Most used techniques for coating fertilizers granules

The coating methods affect the quality of coatings, which is a key parameter to control the nutrients release behavior. With the immersion, the granules fertilizers could be partially dissolved because they are dipped in the coating solution, especially water-soluble fertilizers. Granules could also stick to each other if the solution is very viscous and the coating would be damaged when they are separated after drying. Rotating pan is a good alternative for immersion. The coating parameters of rotating pan would affect the coating quality (dimensions, rotational speed, spray flow rate, etc.). Generally, rotating pan is known by minimizing mechanical damage to the bead and reducing the level of attrition because the granules movement is soft. Consequently, the coating layer is less damaged by the coating process. However, uniform thickness of the coated layer cannot be easily achieved for the entire fertilizer batch unless larger amounts of the coating materials are utilized. The weak coating uniformity and the higher product variability would affect the release rate of nutrients. The release would not be uniform through the coating layers [92,93,95,96]. In the case of fluidized bed, the layer thickness of the film coating is uniform. Nevertheless, aggressive granules movement produces strong mechanical stress to the beads and the attrition, that could affect the quality of the coatings [18,92,95,99].

3.4.2. Coating formulation

Coating formulation governs the release behavior of nutrients and it is managed by the components used and their compatibility, their hydrophilic or hydrophobic nature, their concentrations in the solution and the viscosity.

Hydrophobicity: The hydrophobic/hydrophilic character 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 inside the fertilizer core and decreases the dissolution [47]. Jarosiewicz [47] showed that the release rate of NH_4^+ is three times faster when using the hydrophilic polyacrylonitrile as a coating for nitrogen fertilizer compared to the hydrophobic polysulfone.

***Components compatibility and modifying agents*:** The compatibility between components affects the coating forming quality. If the components are not compatible, two or more phases could coexist in the same coating, which will produce a non-homogeneous film. In most coating formulations; plasticizers, crosslikers or compatibilizers are added to improve the homogeneity of the solution, the flexibility, the tensile strength and the adhesion properties of polymeric membranes [21,22,100]. With these properties, the shell could resist the internal pressure created inside the core in contact with water, and the nutrients would be released slowly without destroying the shell. Niu et al. [89] reported that the presence of the plasticizers in the coating formulation retards the release of ammonium nitrate. They suggested that this fact is related to the formation of films without cracks when plasticizers have been added, which decrease the permeability of water and decrease the release of nutrients. Blending, grafting and copolymerization of different biopolymers between them with synthetics are also used to produce good coatings. Coated urea by natural rubber reinforced by grafting with modified cassava starch (NR-g-ST) has been reported by Riyajan et al. [63]. Capsule coating with only starch was almost released 100% of N within 8h. With the NR-g-ST coating, the capsule released 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 with the increase of the polymer concentration in the coating solution. In fact, higher polymers concentration produces high thickness and low porosity in the coating layers of granules fertilizer [47]. Nui et al. [89] showed that the coating formulations with a 10% (wt/wt) of ethyl cellulose in the coating solution produce lower thickness (49.26 µm) on coated urea, compared to 70.01 µm with 20%. The release of N through thick layer was slower than with thin one. This results are in accord

with those of Pérez et al. [101] who argued that the N release from an ethyl cellulose coated granule depends on the polymer concentration in the formulation. As expected, high concentration of the polymer increases the thickness of the coating film, and delays the release rate of N.

3.4.3. Numbers of layers

Fertilizer granules can be coated by one [39] or many layers [44] using the same coating solution. They can also be coated by two [17,18,29,50,102] or three layers [19] of different solutions, and by the same or different coating techniques. The most commons are simple and double layers. In the case of double and triple layers, the second layer is generally a superabsorbent.

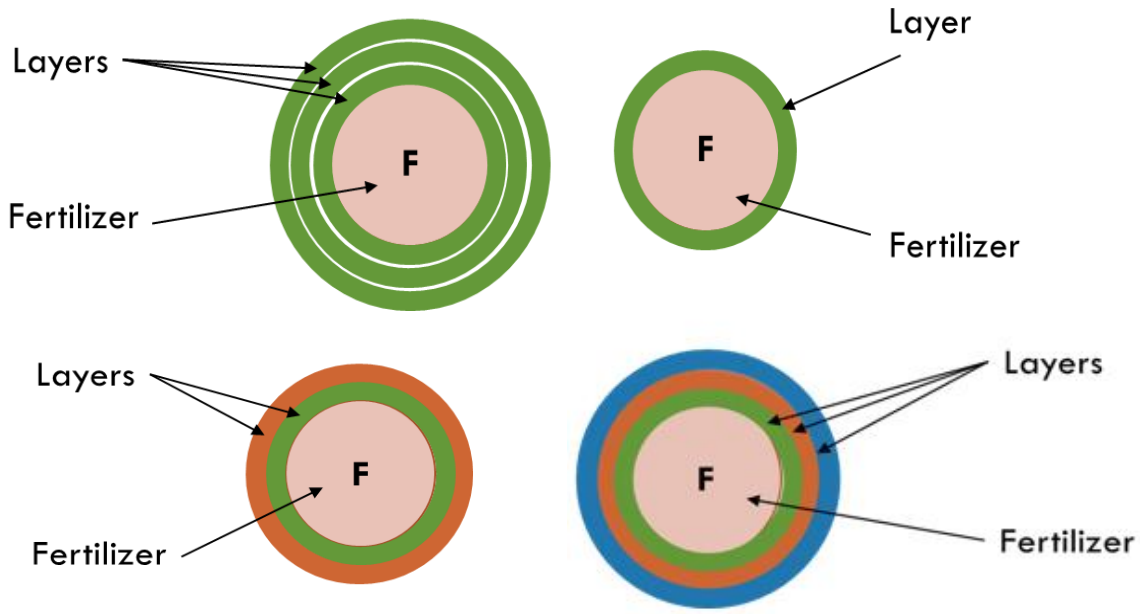


Figure I-4: Simple, double and triple coating schemes

Coated granules by simple coating or multiple coatings using the same coating solution: One layer is made using a technic from those that we previously mentioned in the part 3.4.1. In the case of multiple layers, they are obtained by coating the granule fertilizer and drying it before re-coating until obtaining the desired number of layers **(Figure I-4)**. Generally, the notion of multiple layers using the same solution is related to the immersion technic. The granules are dipping for one, two or more times respectively in the same coating solution. Lubkowski [62] developed a chitosan-based formulation to coat NPK fertilizer by a simple coating. Results show that 64%-96.5% of P have been released in water from coated fertilizer within 5 hours compared to 100% within one hour from uncoated fertilizer. Ahmed et al. [20] also prepared a

chitosan-coated phosphorus fertilizer and studied the effect of layers numbers on the release rate of P. The thicknesses of the double and triple-coated films are approximately 1.5 (96 μm) and 2 (128 μm) times higher compared to the single layer (63 μm) of coating film, respectively. The average thickness of the coating film increases with an increase of the number of coatings. The release rate of P was lower in triple coated granules than in single one, showing the thickness effect on the P release behavior. Jarosiewicz et al. [47,84] also reported that coated NPK granular fertilizer based on cellulose acetate and modifying agent (formamide) released nutrients rapidly after 5h and the slowest release was achieved with a double coating by 18% polymer solution with 5% formamide in the casting solution. They showed that one layer coated NPK with 17% polyacrylonitrile solution released 97.3% of K compared only to 11.7% with three layers of the same solution.

Coated granules by double coatings using two different coatings solutions: In the case of double layers with different coatings solutions, the aim is to ensure several properties through several layers. The first layer is generally dedicated as a physical barrier to nutrients to not go out, and the second one is a superabsorbent capable of absorbing water and releases it later **(Figure I-4)**. 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 in comparison with the single one [47]. Wi et al. [17] developed a double-coated slow-release NPK compound fertilizer (2.36-2.85mm) 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 coated fertilizers was in the range of 2.3-11.9% in 3 days and 64-73.2% in 30 days. These releases are much slower than that of uncoated fertilizer with more than 80% and 87% within only 2 and 5 days, respectively. Ni et al. [103] investigated a multifunctional slow release fertilizer using a matrix of NPK fertilizer with natural attapulgite clay mineral fibers 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 uncoated fertilizers in soil was 98,5% in 12h [104], while the same percentage was released through coated fertilizers in 30 days. A double-coated slow-release NP fertilizer has been reported by Lihua Xie et al. [29] with wheat straw/sodium alginate blends as the inner coating and poly (acrylic acid-co-N-hydroxymethyl acrylamide)/wheat straw superabsorbent composite as the outer coating. The release behavior was investigated in soil. The release of N from the coated fertilizer decreased to the half (40.3%) compared to uncoated fertilizer. For the P release, it was just 42.6% in 30 days from coated NP compared to 66.2% in 5 days from uncoated fertilizer. Wang et al. [50]. 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 inner and outer coating materials. The release rate of nitrogen from the coated fertilizer was 94% within 25 days, which was much slower than uncoated nitrogen fertilizer reported to be 98.5% of N in 12 h [104]. 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 rate of N, P and K through the core (NPK + attapulgite) in soil was fast; 100% in 5 days for N, 93.3%, 94.2 for P and K in 30 days, respectively while the release rate through the double-coated fertilizer was 100% in 20 days for N, 88.2%, 92.4 for P and K in 30 days, respectively. Note that the release rate of nitrogen is the highest one, while the release rate of P is the slowest one, which was in agreement with Wu et al. [18]. To explain why, the ionic mobility and the electronic and steric effects of the K^+ and NH^{4+} ions were compared. Ionic mobility of N and K is very similar (1.000 and 1.001 $m^2\ s^{-1}\ V^{-1}$), they have also the same positive charge value. However, the size of K^+ (1.33A°) is smaller than that of NH^{4+} (1.47A°), and the K^+ ions have a higher surface area charge density to interact with the negatively charged carboxylate ion of the hydrogel layer [19], and then it spreads slowly [18]. Lu et al. [22] investigated an environmentally friendly N mixed with natural attapulgite as the core, starch acetate as the inner coating and the carboxymethyl starch/xanthan as the outer coating. The release rate of uncoated fertilizer was 79.9% in 1 days while decreased to 56.5% by coating the fertilizer with starch acetate only. The addition of the second layer (carboxymethyl starch/xanthan gum) doubled the time taken to release 100% of N from five to 10 days. Wang et al. [69]. developed a biomass-based multifunctional controlled-release fertilizer. The fertilizer based on natural attapulgite, ammonium zinc phosphate and urea, cellulose acetate butyrate and carboxymethyl chitosan-g-poly (acrylic acid)/attapulgite superabsorbent composite were the inner and the outer coating. The release rate of N through uncoated fertilizer in soil was 98.5% in 24h. After coating, 9.2, 53.1, and 81.4% of 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 Zn was released within 30 days. Mingyo et al. [85] reported the production of slow-release membrane- urea fertilizer. The first layer was starch and the second one was acrylic acid and acrylamide. The release rate of N in soil from simple fertilizer was more than 85% in 2 days. However, when the fertilizer was coated by the starch and acrylamide, the release rate decreased more than 8 times.

Coated granules by triple coatings using three coating solutions: Triple coating of fertilizer is made by coating the core using the first solution, and waiting for it to dry before applying the

second, and the same for the third solution **(Figure I-4)**. However, previous studies using three layers from different coating solution are scare. Noppakundilograt et al. [19] developed a trilayered controlled-release NPK fertilizer hydrogel by dipping the NPK fertilizer granules in poly (vinyl alcohol) (PVA) to form the first layer. After drying, PVA-coated fertilizer granules were immersed in chitosan solution and then the obtained PVA-chitosan bilayer coated fertilizer granules were cross linked for 4 days. After that, the third layer were prepared by suspension graft copolymerization of acrylic acid (AA) and acrylamide (AM) to form the poly (AA-co-AM). Results show that the coated NPK fertilizer did not dissolve completely 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%).

All this work has shown the effect that biopolymers play in coating formulations, as well as other coating parameters such as coating technique, thickness of the coating, etc. The majority of works combined formulations of polymers or biopolymers with additives, to coat fertilizers with one or more layers, and with one or different coating techniques. However, testing biopolymers alone without additives or without combining them with others has never been studied. In addition, the use of biopolymers extracted from biomass is rarely tested.

Table I-3: Fertilizers type, polymer materials used as coatings, operating conditions, parameters of coating and nutrients release rate

Reference	Coating materials	Fertilizer	Granule size (mm)	T coating (°C)	Contact time (min)	T drying (°C)	Time drying (min)	Coating methods	Thickness (mm)	Release rate (%)
[63]	Natural rubber (NR)-g-starch (ST)	N	-	-	-	30	72	Immersion	-	**Coated** ST : 100% in 8h NR: 24% in 24h NR/ST blending : 40% in 24h NR-g-ST: 21% in 24h
[62]	Chitosan	NPK	3 -4	85-105	-	-	-	-	0.047-0.5425	**Coated :** 64%-96,5% within five hours
[84]	Cellulose acetate	NPK	3.15	45	-	104	-	Immersion (phase inversion)	0.19	**Coated (single coating)** N: 100% in 5h **Coated (Double coating)** 35% of **N**, 66.5% of **P** and 49.6% of **K** in 5h
[64]	Ethyl cellulose	N	1-2	60	40	70	10	Fluidized bed	0.0333-0.0556	**Uncoated:** 100% in 0,5 h **Coated:** 22%-35% in 6h
[17]	Chitosan	NPK	2.36-2.85	-	-	Room T	320	Rotating pan	-	**Coated** **N**:11.9, 17.8, 73.2% in 3, 5, 30 d **P:** 3.9, 8.2, 64 %in 3, 5, 30 d **K :** 2.3, 6.4, 68 %% in 3, 5, 30
	Poly (acrylic acid)/diatomite-containing urea					70	-	Shaking with powder		
[18]	Chitosan	NPK	2	-	-	Room T	480	Rotating pan	-	**Coated** **N :**14.7, 19.2 and 79% in 3, 5, 30 d **P:** 10.9, 14.3, 62% in 3, 5, 30 d **K :** 12.4, 16.7, 69% in 3, 5, 30 d
	poly (acrylic acid-co-acrylamide)			65	120	70	-	Immersion		
[12]	Cellulose acetate	NPKCuMg	2.0 to 2.3	-	-	60	-	Immersion (phase inversion)	-	**Coated** 4.2, 8.7, 72.4% in 3, 5, 30 d
	poly (acrylic acid-co-acrylamide)/unexpanded vermiculite			65	120	70	-	Immersion		
[103]	sodium alginate	NPK	1-1.3	-	-	-	-	Rotating pan ($CaCl_2$atomization)	-	**Uncoated: N**: 98.5% in 12h **Coated:** 100% of **N**, 81.3 of **P** and 91.1% of **K** in 30 d
	alginate-g-poly (acrylic acid-co-acrylamide)/humic acid			-	-	45	-	rotating pan		
[29]	wheat straw/sodium alginate	NP	1−1.3	-	-	-	-	Rotating pan ($CaCl_2$atomization)	-	**Uncoated** >80% of **N** in 3d and 66% of **P** in 5d **Coated** **N** : 30.5, 40.3, 98.5% in 1, 5, 30 d, **P** : 6.3, 18.7, 42.6 % in 1, 3, 30 d
	poly (acrylic acid-co-N-hydroxymethyl acrylamide)/wheat straw			-	-	-	-	-		
[51]	Guar gum			-	-	-	-	Rotating pan (borax atomization)		**Uncoated:** 100% of **N** in 5 d, 93.3% of **P** and 94.2% of **K** in 30 d

	guar gum-g-poly (itaconic acid-co-acrylamide)/humic acid	NPK	1−1.3	-	-	-	-	Powder adhered on surface	-	**Coated**: 100% of **N** in 20 d, 88.2 of **P** and 92.4 of **K** in 30 d
[69]	cellulose acetate butyrate (CAB)	ZnNPK	1−1.3	-	-	-	-	Rotating pan	-	**Coated (single layer CAB)** 38.3, 85.3, 96.5 % in 3, 15, 30 d **Coated (Triple layers CAB)** 15.4, 70.3, 87.5% in 3, 15, 30 d **Double coated fertilizer** 9.2, 53.1, 81.4% in 3, 15, 30 d
	carboxymethyl chitosan-g-poly (acrylic acid)/attapulgite			-	-	-	-	Rotating pan		
[22]	Starch acetate	N	1−1.3	-	-	-	-	Rotating pan	-	**Uncoated:** 79,9% in 1 days **Coated** with SA: 56.5 and 100% in 1 and 5 d With SA+ CMS/XG: 100 in 10 d
	carboxymethyl starch/xanthan gum			-	-	-	-	Rotating pan		
[71]	Ethyl cellulose	N	1−1.3	-	-	-	-	Rotating pan	-	**Coated:** 8.7 and 100% in 1 and 20 d
	carboxymethylcellulose/hydroxyethylcellulose			-	-	-	-	Rotating pan	-	
[50]	k-carrageenan sodium alginate	N	2-2.5	-	-	30		Rotating pan (Water atomization)	-	**Coated:** 39, 72 and 94% in 2, 5, 25 d
	k-carrageenan -g-poly (acrylic acid)/Celite			-	-	30		Rotating pan	-	
[85]	Starch	N	1-2	-	-	60	-	immersion	-	**Uncoated:** >85 and 90% in 2, 5 d **Coated:** 10, 15, 61% in 2, 5, 30 d
	Acrylic acid & acrylamide			67	120	70	-	Immersion	-	
[19]	Polyvinyl alcool	NPK	-		5	Room T		Immersion	-	**Coated** **N**: 21.1, 33.5, 83.9% in 1, 5, 30 d **P**: 18.3, 22.5, 62.3% in 1, 5, 30 d **K**: 7.4, 9.7, 36.2% in 1, 5, 30 d
	Chitosan			-	-	Room T	240	Immersion	-	
	poly (acrylic acid-co-acrylamide)			70	45	50		-	-	

4. Effect of coated fertilizers on soil & plant

Over the last decades, various polymers have been widely used and have been found very promoting for agricultural application [105–110]. Most work involving polymers coated fertilizers focuses on the rate of nutrient release to water or soil. However, papers investigated the combination effect of polymer/biopolymers and fertilizers (coated CRFs) on soil properties and plant growth are scare, and the work existing does not give details of the formulation and the polymer used. In this part, these works were synthesized and the effect on some soil properties as well as on plant were presented.

4.1.Effect of coated fertilizers on soil properties

4.1.1. Effect of coated fertilizers on soil pH

The soil pH is an important parameter for plant growth because it affects the nutrient availability. Most nutrients are available to plant roots in a soil pH of 5.5–7. Wang et al. [69] prepared a biomass-based CRF including 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 approximately 7. This is because of the large amounts of -COOH and -COO− that can react with the OH^- and H^+ of soil solution, respectively. Another similar work was done using co-granulating beads based of 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 7.09–7.3 from an initial pH values, which varied from 4 to 10. Lombi et al. [24] evaluated the effect of different granular (MAP, DAP, TSP) on soil pH. The initial soils (calcareous and non-calcareous alkaline soil) had a pH of 8.1 to 8.7. Each fertilizer granule was placed on the center of a petri dish with 78 g dry soil (soil density =1.2 or 1.3 g/cm^3, 0.12g-0.15 g P per kg) and sections around granules (0-7.5, 7.5-13.5, 13.5-25.5 and 25.5-43 mm) were recuperated for pH analysis after five weeks of incubation. The change in soil pH was observed near granules (0-13.5 mm) and varied between 0.8 and 0.9 lower than in the unfertilized soils. This decrease in soil pH is probably caused by the low pH of some fertilizers (i.e. TSP), or exchange between

fertilizer cations and H^+ on the soil sorption sites and the nitrification processes. They argued also that the alkaline pH of soil and the large buffering capacity of carbonates in the calcareous soils limited the soil acidification. The type of granular fertilizers used impact the soil pH differently. It was observed by the same authors that the pH of the soil surrounding DAP granules was higher as compared to MAP and TSP. This could be explained by the high pH of saturated solution of DAP (pH=8) compared to those of MAP (pH=3.5) and TSP (pH<3).

4.1.2. Effect of coated fertilizers on soil microbial biomass

Soil microorganisms mediate many important biological processes for sustainable agriculture. They contribute in nutrient cycling, degradation of agrochemicals and pollutants, etc. Soil microorganisms depend on soil organic C for energy and cell synthesis. The addition of carbon-rich polymers may stimulate microorganisms. Studies using biopolymers/polymers as coatings are scare and all are done with polymers-coated N fertilizers without revealing the nature of the used polymer. This is probably because they use commercial coated fertilizers with confidential formulations. Lupwayi et al. [111] showed that a polymer-coated controlled-release urea (at 50–60 kgN/ha) increased the microbial biomass C in the crop rhizosphere to 1131 mg/kg compared to 918 and 621 mg/kg for urea treatment and for control, respectively. This probably means that the nitrogen as well as the C contained in the coated urea was assimilated by the microorganisms. The microbial metabolic quotient qCO_2 was higher for the control treatment (without fertilizer), because soil microorganisms were probably nutritionally stressed. Another work carried out by Xiaoguang et al. [112] observed higher microbial biomass C content in soil treated by polymer-coated urea than urea treatment. However, the soil microbial biomass N content with slow-release urea fertilizers was lower during the seedling stage than urea treatment, but was higher after seedling stage. Inubushi et al. [113] reported that soil microbial biomass N was higher with conventional urea fertilizer (100 kg N/ha) than polymer-coated fertilizer (64 kg N/ha) throughout a rice cropping season. This difference could be related to the presence of high amounts of NH_4^+-N that may have allowed the soil microbial biomass to assimilate more fertilizer N in the presence of dissolved organic C resulting in higher biomass N than in the coated urea treatment. Microbial biomass N was generally higher with deep-side application (5 cm deep) of coated urea compared to the broadcast. As to Chu et al. [114], they reported that controlled release urea (150 kg N/ ha) did not significantly affect the microbial biomass, but had significant effects on soil microbial activities (dehydrogenase activity). This result is in accordance with Acquaye et al. [115] who reported that the thermoplastic polyolefin-coated urea (80 kg N/ ha as deep placement) did not affect the amount of microbial biomass N.

4.1.3. Effect of coated fertilizers on nutrients bioavailability

The coating serves as a protective layer to make soil-fertilizer contact difficult and limit interactions between soil and nutrients (i.e. phosphorus fixation). The nutrients availability in soil may govern the nutrients release. There are only few studies investigating the effect of polymers/biopolymers-coated fertilizers on the nutrients availability in the soil. Garcia et al. [116] reported that lignin-coated TSP (11% coating) increased the plant phosphorus absorption after 30 days by more than 1.5 mg P/kg while uncoated TSP did not significantly change P availability compared to the unfertilized soil. Diez et al. [117] also reported that resin-coated DAPs provide control of P fixation in calcareous soils and maintain the P available for long periods (8 months). Furthermore, McKenzie et al. [118] reported that there was no difference between coated urea and uncoated urea in wheat N uptake while Inubushi et al. [113] argued that coated urea fertilizer induced an increase of rice plants N uptake by more than 45% after 117 days compared to uncoated urea. The same authors justified that by the high solubility of urea and the mode of fertilizers application. In fact, urea was applied on broadcast while coated urea in deep side, which insured a closer proximity of the rice roots and led to more N uptake. As to Zhang et al. [119], they reported that controlled-release urea reduced potential N loss compared to urea. In another work carried out by Cruz et al. [120] on effect of polyurethane-coated DAP fertilizer on P availability in an oxisol, the role of the thickness of the coating on the P availability is crucial. According to the same authors, noncoated and coated DAP with 1.5 and 3.0 wt showed high available P (100-118 mg/kg) within 168 h while coated DAP with 4.5-6 wt% and 7.5-9 wt% showed 50-60 mg/kg and only 0-20 mg/kg of available P within the same duration. This behavior could be explained by the fast release when no or low coating was applied and slow and extended release with moderate or high amount of coating.

For P migration, Castro el al. [121] 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 from the two treatments of P was not significantly different. The majority of MAP and coated MAP's P (>80%) remained within 0–7.5mm from the point of application and the remained P migrated within the 25.5 mm around the fertilizer granule. Lombi et al. [24] et Lawton et al. [122] found the same diameter diffusion of P using different P resources (MAP, DAP, TSP and others) in different water-saturated soils (calcareous, oxisol and loamy soil).

4.1.4. Effect of coated fertilizers on 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. [123] showed that the addition of 0.5 w/w% of cellulose-based superabsorbent to a sandy soil have doubled its moisture content and dramatically improved its

water retention and its water holding capacity of a sandy soil. Similar results have been reported by Tran et al. [124] using 0.5w/w% of starch and xanthan gum hydrogels. 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 biopolymers-coated fertilizers and/or superabsorbents-coated fertilizers also showed an increase on the water retention (WR) and water holding capacity (WHC) of the soil. **Table I-4** summarizes the results of some studies.

Table I-4: Comparison between water-holding capacity (WHC) and water retention (WR) behavior of the soil in presence/absence of polymeric coating

Ref	Fertilizer	Coatings material	Added amount	WHC (%)		WR (wt%) (1-Water evaporation (wt%))	
				Without Coating	With Coating	Without Coating	With Coating
[125]	NPK	P(acrylic acid-co-acrylamide)/kaolin	2 g of fertilizer mixed with 200g dry soil)	28.2	40.8	7 after 10 days 0 after 20 days	23.7 after 10 days 14 after 20 days
[71]	N	carboxymethylcellulose/ hydroxyethylcellulose	-	41.5	54	0 after 4 weeks	30.8 after 15 days
[12]	NPKMgCu	Cellulose acetate, poly (acrylic acid-co-acrylamide)/unexpanded vermiculite	2 g of fertilizer mixed with 200g dry soil	28.2	40.3	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
[18]	NPK	Chitosan, poly (acrylic acid-co-acrylamide)	2 g of fertilizer mixed with 200g dry soil	30.2	40.3	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
[50]	N	k-carrageenan sodium alginate, k-carrageenan -g-poly (acrylic acid)/Celite	-	-	59	-0 after 10 days	113.5 after 0 days 62 after 10 days
[17]	NPK	Chitosan, Poly (acrylic acid)/diatomite-containing urea	2 g of fertilizer mixed with 200g dry soil	29.1	39.8	44 after 15 days 5.5 after 30 days	56.5 after 15 days 22 after 30 days
[29]	NP	wheat straw/sodium alginate, poly (acrylic acid-co-N-hydroxymethyl acrylamide)/wheat straw	-	-	63.2	-	-
[69]	ZnNPK	cellulose acetate butyrate, carboxymethyl chitosan-g-poly (acrylic acid)/attapulgite	1-3 g of fertilizer mixed with 200 g dry soil	38.5	69	5.1 after 15 days 0 after 18 days	49.8 after 15 days 44.1 after 18 days
[85]	N	Starch, Acrylic acid & acrylamide	2 g of fertilizer mixed with 200g dry soil	29.3	41.8	49 after 12 days 5 after 21 days	64.5 after 12 days 27 after 21 days
[102]	N	Olyurethane, chicken feather protein, acrylic acid,and N,N′-methylenebisacrylamide	2 g of fertilizer mixed with 200g dry soil	-	-	17.2 after 28 days	34.5 after 28 days
[126]	N	poly(dimethylourea phosphate), wheat straw , acrylic acid, 2-acryloylamino-2-methyl-1-propanesulfonic acid, and N-hydroxymethyl acrylamide	1-2 g of fertilizer mixed with 150 g dry soil	33.1	46.8	41 after 15 days 6.5 after 30 days	65.6 after 15 days 24.8 after 30 days

The use of formulations based-biopolymers as coating agents showed good improvement on soil water-holding capacity and water retention behavior. All formulations are composed on a mixture, copolymerization or grafting of polymers/biopolymers and additives (plasticizers, crosslinkers, compatibilizers, etc). However, the use of testing biopolymers derived from biomass alone or in combination with other polymers/biopolymers has never been studied.

4.2.Effect of coated fertilizers on plant

Over their undeniable role in slow/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 plants growth. In this regard, Niekraszewicz et al. [127] showed that biopolymers-based formulations (chitosan and hemicellulose) improved the growth of the rooted seedling compared to untreated ones.. These formulations have also shown an antiviral action. This action is done according to two phenomena: (1) by blocking the virus-specific receptors resulting from the affinity of the polymers to these receptors, (2) by inducting immunity system against pathogens. In the same context, Kumaraswamy et al. [128] have recently reported that chitosan can be used as either a biostimulant or biopesticides to control a leaf spot disease of maize by 38.88% and enhance yield. In the other hand, Ramirez et al. [129] report that adding chitin and its derivatives to the soil promote the growth and the activities of many beneficial micro-organisms (chitinolytic microbes), which act as a biological control against many agents responsible for plant infections and diseases. In this sense, Sharp [130] reports that the efficiency of treatment based on chitin was comparable to that obtained with current synthetic pesticides. According to the same author, this behavior can be explained by the fact that chitin and its derivatives have been shown to be toxic to pests and plants pathogens. Similar results were observed for biodegradable hydrogels based on cellulose that enhanced plant growth [123]. Recently, the effect of vegetal biopolymer as biostimulant on root growth and on resistance toward plant stress was investigated [131]. The findings of this study demonstrated that vegetal biopolymer-based biostimulant promoted plant growth and protect plants from both abiotic and biotic stress factors.

Despite efforts devoted to evaluate the effect of biopolymers on plant, only few papers investigated the effect of the combination of biopolymers/polymers and fertilizers (CRFs) on plant. To our knowledge, some works were done using polymers-coated fertilizers but no work has specified if coatings were based on biopolymers and/or synthetic polymers. Qian et al. [132] compared the effect of conventional MAP granules and polymers-coated CRFs on wheat, canola, mustard, flax, yellow pea and alfalfa yields. Field experiments were conducted in a P-

deficient brown soil. Results showed that the CRFs increased the tolerance of crops to high rates of seed row placed P, with rates of 80 kg P_2O_5 ha^{-1} placed in the seed row [132]. Tian et al. [133] investigated the effect of a NPK coated fertilizer, with no details about the coating nature. Field experiments were conducted for early ripening rapeseed in a red-yellow soil. The same amounts of noncoated fertilizer (control) and coated fertilizers (CRFs) were applied. The comparison of plant height first branch numbers, pod numbers, stem dry weight, and pod dry weight between the two treatments revealed that CRFs gave higher seed yields (+14.51%) than control [133]. Polymer-encapsulated sulfur-coated urea was compared to the standard fertilizer by Landis et al. [134]. Tests were performed on red pine, jack pine, white spruce, and other conifers. Results showed that seedlings were larger with fewer culls in the case of CRFs. In the other hand, McKenzie et al. [118] reported that there was no difference between the polymer-coated urea and noncoated urea in grain yield and grain protein concentration when fertilizers were side-banded in the fall, whereas the use of coated urea was highly effective for reducing seedling damage caused by seed row application of urea. This finding is also reported by Middleton et al. [135], who argued that coated urea did not injure seedlings even when applied in large quantity. Furthermore, Zhang et al. [119] reported that the polymer controlled-release urea had no effect on barley grain yield but increased its protein content compared to urea.

5. Objectives and research strategy of the thesis

5.1. Objectives and hypotheses

Despite the amount of work done on coated fertilizers, the effect of the origin and the nature as well as the structure of biopolymers are rarely taken into account. We also lack information on the possibility of using biopolymers derived from biomass and organic waste as efficient coatings. Another lack of knowledge concerns the effect of polymeric coated–fertilizers on soil properties. Few works addressed that issue and in the majority of cases, the type of polymer is not even mentioned. This pathway needs to be explored further.

The objectives of the present thesis is to study whether the phosphate fertilizers coated with lignin extracted from olive pomace, and other commercial biopolymers from seaweeds or lignocellulosic materials as well as plasticizers are endowed with dissolution and degradation characteristics in soil that could improve their efficiency. Another main objective is to bring new understanding elements on the relationship between the coating agents' properties and the phosphorus release. We started by formulations formations and their characterizations, then we coated phosphorus fertilizers and finally we evaluated the phosphorus dissolution in water and soil (**Figure I-5**).

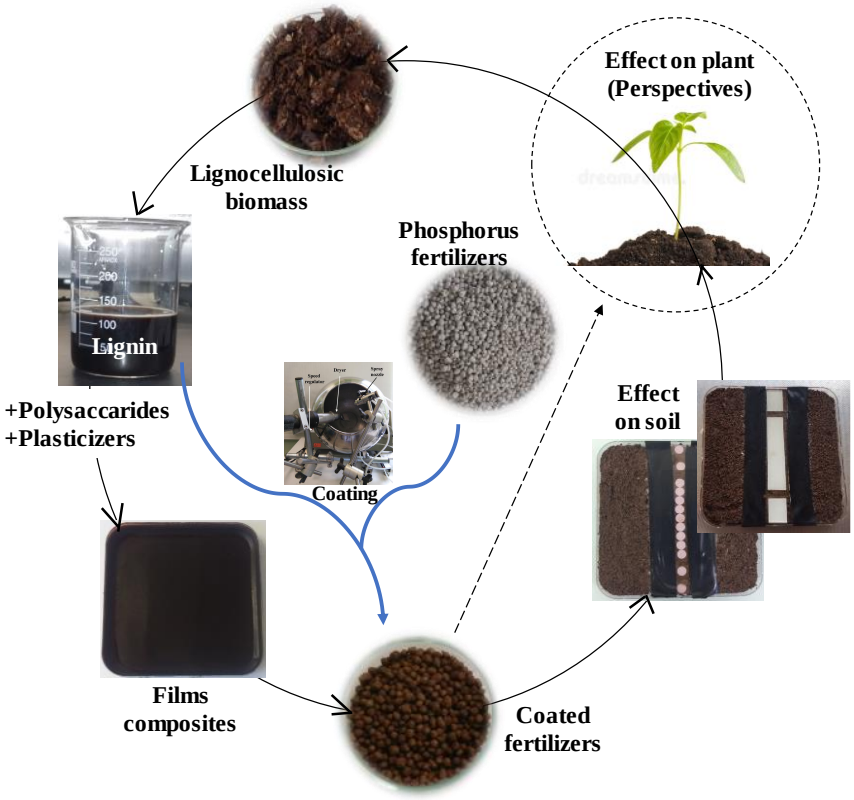


Figure I-5: Overall scheme of the main steps of the thesis

These objectives were addressed by answering the following scientific questions and considering several hypothesis:

Question 1: Does the nature of the biopolymers influence the properties of the coating agent and the release behavior of phosphorus in water?

Hypothesis 1: The hydrophilic/hydrophobic nature of the biopolymer, its structure and its origin would affect the surface properties of the coatings, porosity, their water absorption, etc. and then would influence the release behavior of P from coated phosphorus fertilizer.

Question 2: Does the addition of plasticizers in the coating formulation affect the properties of the coating agent and the release behavior of phosphorus in water?

***Hypothesis 2*:** The plasticizer would give more elasticity and plasticity to the coating, which would give it more resistance to the osmotic pressure created inside the granule in contact with water, and therefore more chance of not bursting (catastrophic release).

Question 3: Does the coating thickness affect the phosphorus release rate?

Hypothesis 3: When the thickness of the coating is thick, the path followed by the phosphorus through the membrane to the outside of the granule would become longer and therefore the rate of phosphorus release would slow down.

Question 4: Do coated fertilizers have a different dissolution behavior in soil compared to uncoated fertilizers?

Hypothesis 4: A uniform diffusion will be occurred in a circular radius around the fertilizer, with low diffusion with coated TSP compared to uncoated TSP due to the barrier effect of the coating.

Question 5: Do coated fertilizers have a different effect on soil available P and microbial P compared to uncoated fertilizers? Does the coating stimulate soil microorganisms to consume phosphorus?

Hypothesis 5: For available P, the rate of P release could affect the bioavailability of P in the soil. The available phosphorus released by rapid-release fertilizers would be higher in the first few days, exceeding the plant's needs. The excess not absorbed by the plant would then be adsorbed by soil colloids or fixed by minerals, resulting in its unavailability. In contrast, coated fertilizers would release phosphorus slowly. The plant would then take advantage of the available phosphorus according to its needs without phosphorus being fixed by the soil (due to the shorter contact time between P and soil). For microbial P, Polymeric coatings applied to the soil are rich in carbon. Decomposition of these coatings by microorganisms would result in phosphorus consumption to balance the stoichiometric ratio of C/P microorganisms, and therefore microbial phosphorus would be higher in the presence of the coating.

Question 6: Do coated fertilizers affect the recovery of applied phosphorus than uncoated fertilizers?

Hypothesis 6: Recovery of applied phosphorus would be important for uncoated fertilizer and specifically on the area closest to the fertilizer location. The concentration of water-soluble phosphorus would be high in the soil immediately around the granule, and the phosphorus would precipitate into the granule itself, resulting in a low spatial distribution of phosphorus. Unlike coated fertilizers, the concentration of water-soluble phosphorus would be low and no saturation would be occurred in the granule environment, allowing phosphorus to migrate away from the granule.

5.2.Research strategy

For questions 1, 2 and 3, we have adopted two strategies (**Figure I-6**); the first consists in forming composite films based on biopolymer formulations from different origins. These films have been characterized for their structure, hydrophobicity, mechanical properties, thermal and water stability, etc. The second approach consists in coating TSP phosphate fertilizers with these same formulations using a coating system that we have developed. Then, these fertilizers have been characterized for their morphology, thickness of the coatings, hygroscopicity and phosphorus release in water. Film formation was adopted because some characteristics were

not possible to do on the fertilizer granule because of its size and shape (i.e. attraction tests, hydrophobicity tests by contact angle). For the questions 4 to 7, the best coated fertilizers according to their slow phosphorus release were selected and soil experiments were performed. Experiments were carried out in the laboratory in petri dishes to study the effect of coated fertilizers on soil pH and on soil phosphorus balance (available P, microbial P and total P) **(Figure I-6)**.

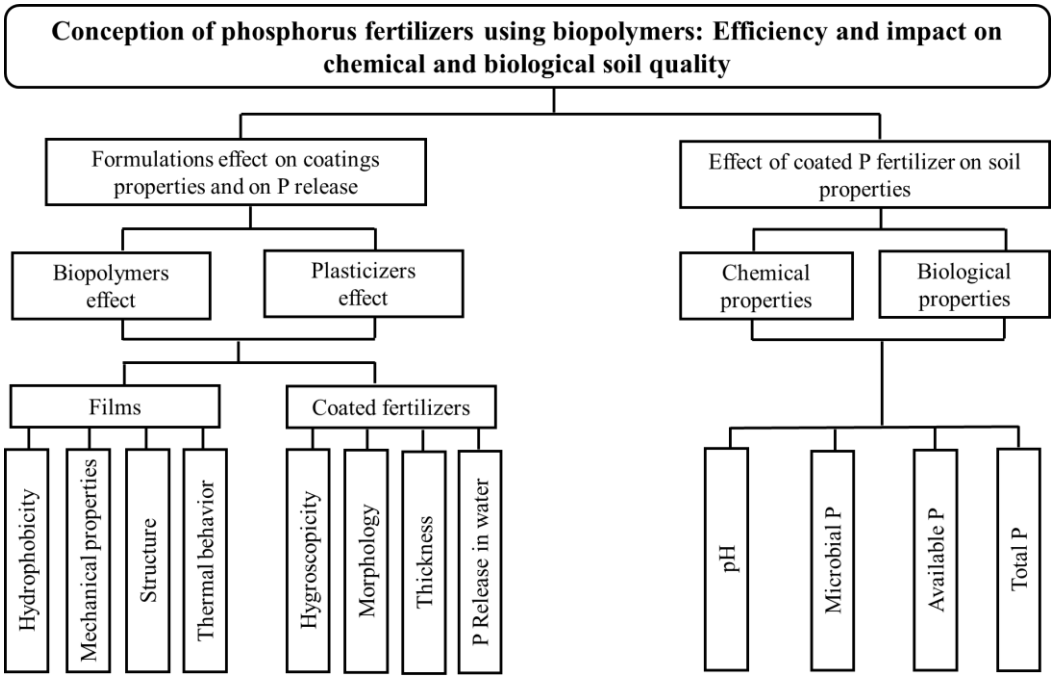


Figure I-6: Schematic diagram of the research strategy

This thesis is composed of five chapters, structured as follows:

Chapter I, entitled "literature review", describes the scientific context of the thesis. The first part describes the state of the art of CRFs, materials and techniques used to produce coated CRFs as well as parameters controlling the release behavior of nutrients through coatings. The second part presents the effect of coated CRFs on some soil properties and plant growth. **Chapter II**, entitled "Materials and Methods", describes the different experimental protocols used in this work, physico-chemical analysis techniques and the statistical analysis performed on the data acquired. The results and the discussions of the thesis are divided into two chapters (III and IV). **Chapter III** aimed to answer the three first scientific questions mentioned previously. It investigated the effect of biopolymers origin and nature as well as plasticizers addition on coatings properties and on phosphorus release in water. **Chapter IV** investigated the effect of coated phosphorus fertilizer on some chemical and biological soil properties (Questions 4 to 7). Finally, an overall conclusion of the work includes major results and proposes some perspectives for further research work.

CHAPTER II. Materials and methods

Chapter II

This chapter depicts materials used and the experimental section of this thesis. Biomass and different commercial biopolymers and plasticizers used with their specifications were presented. The experimental section is divided into two parts: the first one is devoted to the formulations, the films preparation, the P fertilizers coating and the characterization techniques used to study the properties of produced compounds. The second part shows the experimental approach in the soil and the processes employed.

1. Materials

1.1.Lignocellulosic biomass and lignin extraction

Olive pomace (OP) was used as a starting material for lignin extraction. OP was provided from a Moroccan olive press (Tadla region). The substrate was air-dried, and its particle size was reduced to 1 mm with a knife milling (Retsch SM100). OP was mainly composed of olive stones, skin and pulp. This lignocellulosic biomass was chosen because it is abundant, undervalued in Morocco and mainly rich in lignin (LG). Moreover, it contains other interesting elements such as cellulose, hemicellulose, proteins and lipids [136]. LG was picked out as the principal element for P fertilizers coating because it is a renewable, biodegradable, amorphous and relatively hydrophobic biopolymer. In addition, lignin is rich in carbon, which could contribute to increasing the soil organic matter content.

For alkaline lignin extraction, a total of 200 g equivalent dry of ground OP biomass was immersed in 1.5 L of distillated water with 0.16 M NaOH. The mixture was reacted in a beaker and maintained at 70°C with stirring (300 rpm) for 2 h. The concentrated alkaline solution was separated by centrifugation (10 min, 4000 rpm). Lignin is ionized by deprotonation in a highly alkaline solution , in which it becomes partly dissolved and interacts with sodium ions in the liquor [137]. The concentrated black liquor containing lignin and residues of dissolved cellulose, and hemicellulose was used directly for coating formulation and film composite preparation.

1.2.Polysaccharides and plasticizers

Besides LG, some commercial polysaccharides were used to prepare our different formulations composites for P fertilizer coating. We used alginates (AL) (CAS: 9005-38-3) from brown algae, carrageenan (CR) (CAS: 1114-20-8) from red algae and carboxymethyl cellulose (CM) (Mw~700.000, CAS: 9004-32-4) from wood pulp. They were purchased from Sigma-Aldrich. The choice of these polysaccharides is based on the availability and dissimilarity of their basic materials (algae and wood), their ability to form films and their high water absorption capacity

[50]. Plasticizers are generally added to the film-forming polymer to improve the mechanical properties of the coating shell. In this work, three plasticizers were tested: glycerol from animal fats or palm / coconut oils (CAS: 56-81-5, Mw=92.09g/mol), polyethylene glycol from petroleum-derivatives 200 (CAS: 25322-68-3, Mw=200 g/mol) and polyethylene glycol 2000 (CAS: 25322-68-3, Mw=2000 g/mol). All purchased products are used without any further purification.

1.3.Phosphorus fertilizer

Triple superphosphate (TSP) was chosen as P fertilizer to coat. It is a granular phosphate fertilizer with 46% P_2O_5, was produced and offered by OCP Group, Morocco.

2. Experimental approaches

2.1.Part 1: Formulations and coating

2.1.1. Preparation of formulation composites

Formulations and film composites were prepared using lignin (LG), k-carrageenan (CR), sodium alginate (AL), sodium carboxymethyl cellulose (CM), glycerol (GL), polyethylene glycol (PEG) 200 et 2000 in different ratios (**Table II-1**). Black liquor (33.34 g/l LG) obtained after alkali treatment of OP was used directly. Polysaccharide solution was prepared by mixing the product in powder form (0.5 w/w%) with distilled water under constant stirring for 2 h. The lignin-polysaccharide-based composite was prepared as follows: 80% of LG was mixed with 20% of polysaccharide (w/w). The lignin-polysaccharide-plasticizer-based composite was also prepared similarly to the lignin-polysaccharide composite, except for the addition of 30% plasticizer to the mixture. The choice of 30% of plasticizers was made for two reasons: i) according to the studies of Basiak et al. [138,139] who tested different ratios of plasticizers: polysaccharide (glycerol: starch) and concluded that 30% of the plasticizer is the minimum concentration required to obtain ductile and not brittle films. ii) we doubled the percentage of the plasticizers compared to polysaccharides in order to study the effect of plasticizers without being hidden by polysaccharides effect. All formulations were stirred overnight at room temperature. The same formulations were used for film composite preparation and TSP coating. For the film preparation, the mixtures were deposited onto square petri dishes (12 cm*12 cm), and the water was evaporated by drying overnight at 40°C.

Table II-1: Composition (wt%) of different prepared formulations					
Polymers-based formulations	LG (%)	AL (%)	CM (%)	CR (%)	Plasticizer (%)
LG	100	0	0	0	0
AL	0	100	0	0	0
CM	0	0	100	0	0
CR	0	0	0	100	0
LG-AL	80	20	0	0	0
LG-CM	80	0	20	0	0
LG-CR	80	0	0	20	0
LG-CR-GL	55	0	0	15	30
LG-CR-PEG200	55	0	0	15	30
LG-CR-PEG2000	55	0	0	15	30

2.1.2. Preparation of coated TSP fertilizers

Granules of TSP fertilizer (50 g) were sieved to select homogeneous granules with diameters of 2-3 mm (the dominant seize by more than 80 wt%) and then placed into a rotary drum (12 rpm, capacity of 11 L) developed in our laboratory (**Figure II-1**). The distance between the spray nozzle and the center of the rotary drum was 25 cm. Fifty grams of TSP granules were covered with a layer of different formulations (3 g) by spraying at regular time intervals. The mass ratio of TSP/polymer was 15/1. Then, the coated TSP granules were continuously dried in the rotary drum by a hot air stream (65 °C). To study the effect of the solution concentration on coating thickness and phosphorus release behavior, the mass concentration of some coating solutions was tripled (the ratio of TSP/polymer was 5/1)

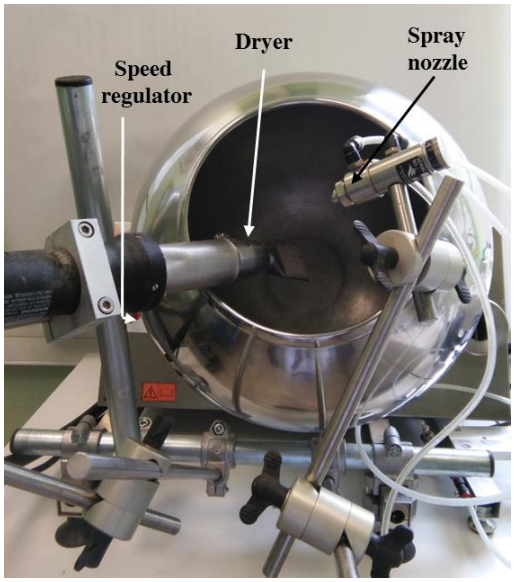


Figure II-1: Rotary drum for coatings developed in this study

2.1.3. Characterizations and analytical methods

- **Determination of carbohydrates and Klason lignin content, and C, H, N, S composition**

The structural-carbohydrates (glucose, xylose and arabinose) content from cellulose and hemicelluloses of OP was determined using a high-performance liquid chromatography (HPLC). HPLC allows the separation or purification of one or more compounds from a mixture in order to identify and quantify them. Before HPLC determination, the first step was acid hydrolysis of biomass following the method of Sluiter et al. [140]. Briefly, crashed samples (80 mg) were first hydrolyzed with 0.85 ml of 11.95 M H_2SO_4 acid for 1 h at 30 °C, then diluted with 23.8 ml of distilled water and kept at 121°C for 1 h. After that, the obtained suspension was filtered. For sugar content determination (glycose, xylose and arabinose), the soluble phase was injected on HPLC system equipped with a column (HPX-87H, BioRad, USA) and a refractometer detector at 40°C using 0.005 M H_2SO_4 as eluent with a flow rate of 0.3 mL/min. The calculation of % cellulose and % hemicellulose was performed using following equations [140]:

$$\%Cellulose\ \left(\frac{g}{100\ g\ simple}\right) = \frac{\text{Glucose}\left(\frac{\text{g}}{\text{L}}\right)*\text{Vtot}}{\text{Mini}*1.11} \qquad \textbf{Equation 3}$$

$$\%Hemicellulose\ \left(\frac{g}{100\ g\ sample}\right) = \frac{(\text{Xylose}\left(\frac{\text{g}}{\text{L}}\right)+\text{Arabinose}\left(\frac{\text{g}}{\text{L}}\right))*\text{Vtot}}{\text{Mini}*1.13} \qquad \textbf{Equation 4}$$

where V_{tot} is the total volume of ultrapure water, M_{ini} is the initial weight of the crushed biomass, 1.11 is the conversion factor between glucose and cellulose and 1.13 is the conversion factor between monomers (xylose, arabinose) and hemicellulose. After that, the remaining solid phase (insoluble phase) was lignin. It was dried at 105°C and weighed, and % lignin was calculated. Three samples were characterized, and the reported results are average values. For C, H, N, and S measurements for OP and lignin, they were performed by elemental analyses (Analyzer vario MICRO V4.0.2, France).

- **Thermogravimeric analysis of film composites**

The lignin, the polysaccharides and the plasticizers as well as the formulations composites were analyzed for their thermogravimetric behavior using TGA, Mettler Toledo. TGA measures a change in a sample mass under a temperature variation (heating or cooling) or over a temperature range, in a controlled atmosphere. The maximum temperature is selected so that the sample weight is stable at the end of the experiment and all reactions are completed. TGA was conducted following the program below (**Table II-2)**. The moisture, volatile matter and fixed carbon were determined under nitrogen. N_2 is an inert gas that does not interfere during

degradation, showing the effect of heat degradation without oxidation. The amount of ash was determined as the remaining mass after combustion (complete degradation in oxidative environment).

Table II-2: TGA programs for film composites under nitrogen and then air flow of 50 ml/min				
Segment	Program			
1	Dynamic	25°C-110°C	5°C/min	N_2
2	Isotherm	110 °C	1h	N_2
3	Dynamic	110°C - 900°C	5°C/min	N_2
4	Isotherm	900°C	30min	N_2
5	Isotherm	900	1h	Air

The graph model (**Figure II-2**) presents the different loss steps in samples mass corresponding to each reached temperature.

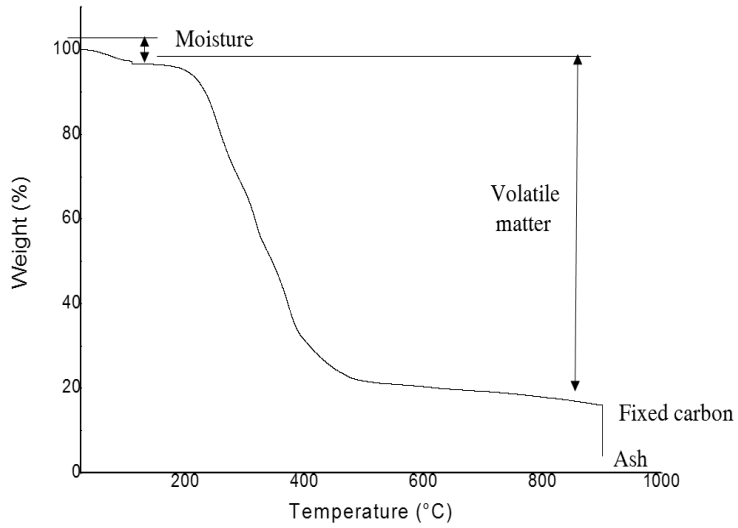


Figure II-2: TGA graph model

- **Structural analysis of lignin, polysaccharides, plasticizers and films composites**

The extracted lignin, commercial polysaccharides and plasticizers as well as the formed film composites were analyzed for their structure using Fourier transform infrared spectroscopy (FTIR). FTIR is based on the absorption phenomenon that occurs when infrared radiation passes through the sample. Depending on the different vibrations modes in the material, the Infrared radiation is absorbed selectively. When a molecule or group constituting the material is excited to its own vibrational state, it absorbs the incident energy, allowing the identification of bonds present in the material. FTIR was performed on a Tensor 27 apparatus equipped with ATR

accessory. The experiments were carried out in the 4000-400 cm^{-1} region with a resolution of 4 cm^{-1} and an accumulation of 16 scans. The FTIR spectra were acquired in absorbance mode.

- **Contact angle measurements (CA)**

The hydrophobicity of the composite films was evaluated using contact angle (CA) measurements between water drops (deposited on the film surface) and the film surface (**Figure II-3**). The hydrophobic surface corresponds to a contact angle > 60°, while a contact angle < 60° corresponds to a hydrophilic surface (**Figure II-3**) [141]. Before contact angle measurements, films were cut into small rectangles (0.5 cm*2 cm), and their support sides were glued to glass slides using double-sided tape. Samples were equilibrated for 5 days at different level of relative humidity (RH) in humidity-controlled rooms. Contact angle measurements were realized with a goniometer (Digidrop, GBX, France) equipped with a diffuse light source and a CCD camera (25 frames/sec). A droplet of ultrapure water (~3 µL) was deposited on the film surface with a precision syringe (Teflon needle, 0.82 mm external diameter). The method is based on image processing and curve fitting for the contact angle. The video was analyzed frame-by-frame with GBX software to determine the contact angle as a function of time [141,142]. Three measurements were performed on each sample.

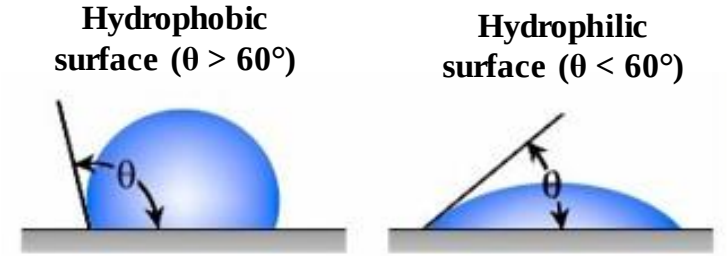


Figure II-3: Schematic diagrams of contact angle measurements [141]

- **Mechanical properties measurements**

The film elasticity (tensile modulus EM), tensile strength (TS) and elongation at break (EB) were studied (**Figure II-4**) using tensile tests. Tests were performed on films using a texture analyzer (TA. XT plus). The tensile specimens were cut into rectangles (80 mm in length and 10 mm in width). The gauge length was fixed at 30 mm, and the speed of the moving clamp was 5 mm/min [143]. Measurements were carried out at room temperature. At least three replicates by samples were characterized, and the reported results are average values with standard deviation.

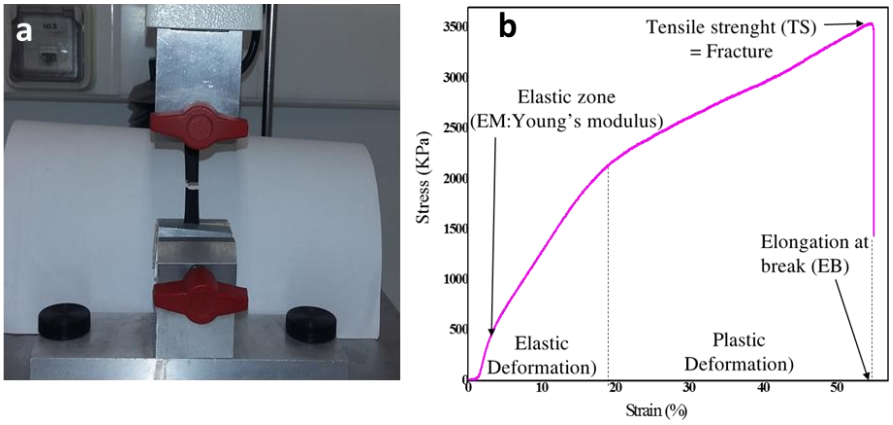


Figure II-4: (a) Tensile tests and (b) tensile tests graph model for film composites

- **Morphology and thickness measurements of films**

Coated TSP were observed using a tabletop scanning electron microscope (SEM) (Phenom ProX, Phenom-World) with a backscattered electron detector (acceleration voltage of 10 kV, mode image). Three granules of each type of coated TSP fertilizer were randomly chosen. These granules were cut in half with a razor blade and fixed on a support. The thickness measurements of the coating layers were performed at three different areas on each half granule (3 replica x 3 areas = 9 measurements).

- **Water absorption of coated TSP**

Coated TSP granules were dried at 50°C in a vacuum oven in the presence of P_2O_5 drying up to weight stabilization . Then, they were conditioned in humidity-controlled rooms at different level of relative humidity (RH). The water absorption of coated TSP was monitored for 3 days [16]. Samples were weighed after each 24 h, and the absorbed water was determined by the weight difference between dried and conditioned samples. All the determinations reported here were performed in triplicate.

- **Slow-release behavior of coated TSP in water**

For release experiments, uncoated and coated fertilizers were equilibrated for 3 days at 60% RH. Then, 0.25 g of each type of coated TSP was immersed in 50 ml of distilled water in glass bottles. The bottles were conditioned at a constant temperature of 25°C. After 15 min, 1 and 6 h, and 1, 2, 3, 4, 5, 7, 10, 15, 20, 24 and 30 day, 1 mL of the solution was sampled for phosphorus concentration determination, and an additional 1 mL of distilled water was added to the bottle to maintain a constant volume. All the release experiments were carried out in triplicate. The phosphorus concentration was determined using the colorimetric molybdenum vanadate method [47]. The colorimetric dosing is performed on DIALAB ELx808 absorbance microplate

reader spectrometer at 450 nm after adding a vanadomolybdic reagent to the sample resulting in the formation of a yellow chromophore complex (phosphomolybdate-vanadate-yellow) and after performing a calibration external with the standard range.

The phosphorus release amount at each time was obtained by **Equation 5** proposed by Rashidzadeh et al. [36] and expressed in relation to the phosphorus concentration and total weight of phosphorus contained in the TSP fertilizer.

$$CR\ (\%w/w) = \frac{V_e \sum Cp_i + V_0\ Cp_0}{mp_0} * 100 \qquad \textbf{Equation 5}$$

where CR is the cumulative amount of phosphorus release (%) from the TSP fertilizer, *Ve* is the sampling volume, V_0 is the initial volume of release media, Cp_i and Cp_0 are the phosphorus concentrations (mg/ml), *i* is the sampling times, and mp_0 is the total weight of phosphorus contained in the TSP fertilizer.

2.2.Part 2: TSP dissolution in soil

2.2.1. Soil setting

The soil was sampled at Mauguio INRAE experimental station in Southern France (3°58'39.898" E, 43°36'45.576" N) (**Figure II-5**). The regional climate is typical Mediterranean with a mean annual temperature of 15.64 °C and 650 mm of annual precipitation. The soil was taken in October 2019 from the top 20 cm in four subsamples of an agricultural plot cultivated since more than 20 years with annual crops. At the time of sampling, the crop was chickpea. The soil sampled was air-dried, sieved to 2 mm, homogenized and stored at 4°C. The soil physical and chemical characteristics are summarized in **Table II-3**.

Figure II-5: Location of the sampling site

Table II-3: Physical and chemical characteristics of the soil	
Soil property	Value
Clay $g.kg^{-1}$	152
Fine silt $g.kg^{-1}$	111
Coarse silt $g.kg^{-1}$	208
Fine sand $g.kg^{-1}$	240
Coarse sand $g.kg^{-1}$	287
Total C $g.kg^{-1}$	13.4
Total N $g.kg^{-1}$	1.21
Total P $g.kg^{-1}$	0.59
Organic P $g.kg^{-1}$	0.16
Organic carbon $g.kg^{-1}$	13.1
Organic matter $g.kg^{-1}$	22.6
$CaCO_3$ $g.kg^{-1}$	2.0
CEC cmol+. kg^{-1}	9.4
pH (water)	7.59
WHC(%)	42.7

2.2.2. Preparation of petri dishes containing soil and fertilizers

Twenty petri dishes (12 * 12 cm^2) were loaded with 171.5 g equivalent dry soil, adjusted to 60% water holding capacity (WHC) and water was added by carefully spreading 31 ml of distilled water over the soil surface with a pipette. The petri dishes were closed with a lid and pre-incubated for one week at 25°C in the dark to stabilize soil microbial activity, with a control of moisture and readjustment if necessary to maintain 60% WHC. Fertilizer treatments were: uncoated granular triple superphosphate (TSP), TSP coated with lignin (lignin@TSP), TSP coated with lignin-carrageenan (lignin-carrageenan@TSP) and a control (soil without any treatment). Granules with almost the same mass (39.3±0.1 mg, 9.8 mg of P) were selected and one granule of each fertilizer treatments was placed in the center of the petri dish. Each with five replicates. For coated TSP, the coating mass and the moisture were taken into account in the calculations so that the amount of P was the same for all coated and uncoated granules. Granules were pushed a few millimeters (1-2 mm) into the soil and a little amount of soil was placed on the top of the granules and on their sides to obtain flat surfaces.

2.2.3. pH measurements

pH mapping of the soil with or without fertilizers were performed using optodes. An optode is a chemical and optical sensor composed of two parts: a chemical part (dye), in contact with the sample, and an optical part that records the signal emitted by the chemical sensor [144]. It is a promoting technique to obtain information about pH, O_2 and CO_2 gradients in soil systems in a non-invasive and reversible way and to study rhizosphere processes at the microscale. Most pH

optodes contains analyte-sensitive and analyte insensitive dyes indicators and are based on the reversible changes of luminescence properties of a fluorescent probe [145,146]. The phenomenon of fluorescence being reversible, temporal monitoring can be carried out without disturbing the sample. Several types of optodes exist depending on the signal-recording mode and the output data format. A distinction is made between fiber optic measurements giving information at a single point, and image measurements giving a 2-D data matrix with a spatial dimension. We used both systems named in this paper: spot optodes for fiber optic measurement and planar optodes for imaging approach.

For spots system, the principle of measurement is based on dual lifetime referencing (DLR) method. This method requires two luminophores; luminescent standard (analyte-insensitive) and fluorescent pH indicator with different lifetimes, overlapping excitation and emission spectra [144]. An optical fiber was used to transfer the excitation light to the spot sensor and to return optical signals to the detector. The difference between signals of the indicator fluorophore and the reference luminophore is converted into a phase angle φ [145,147]. This angle is then converted to pH values based on the calibration curve using **Equation 6** [145].

$$\mathrm{pH} = \mathrm{pH0} + \mathrm{dpH}.\,\mathrm{Ln}\left(\frac{\varphi_{\min} - \varphi_{\max}}{\varphi - \varphi_{\max}} - 1\right) \quad \textbf{Equation 6}$$

where φmin and φmax represent the minimum and maximum range of φ. dpH and pH0 give the slope and inflexion point of the sigmoidal curve, respectively

For planar optodes system, measurements were based on intensity ratiometric method. This method requires a non pH-sensitive and a pH-sensitive fluorophore with different optical properties [144]. The first fluorophore emits in the green part of the spectrum whereas the second emits in the red. In the presence of protons, the balance of the protonated/deprotonated forms of the fluorescent probe is altered. This chemical reaction modifies its fluorescence intensity. A camera connected to a PC was used to detect the fluorescence signals of the foil. Digital images were split into R (red), G (green) and B (blue) images using an image processing software. The ratio between red and green images were converted to pH values based on the calibration curve. The relationship between the measured ratio R and the corresponding pH value is sigmoidal, and can be mathematically described by the **Equation 7** [146].

$$\mathrm{pH} = \mathrm{pH0} + \mathrm{dpH}.\,\mathrm{Ln}\left(\frac{\mathrm{R}_{\min} - \mathrm{R}_{\max}}{\mathrm{R} - \mathrm{R}_{\max}} - 1\right) \textbf{ Equation 7}$$

where R_{min} and R_{max} represent the minimum and maximum range of R (green / red ratio). dpH gives the slope of the curve and pH0 the acid dissociation constant of the indicator dye in a specific system .

Planar optode and spot were purchased from PreSens GmbH ®. Planar optode (product code: HP5R – PreSens GmbH, pH range 5.5-7.5) using imaging system (VisiSens TD) and spots (product code: SP-LG1-SA – PreSens GmbH, pH range 4-7.5) using the optical fiber (pH-1 SMA LG1) **(Figure II-6)**. Image processing was performed with the open source software ImageJ (https://imagej.nih.gov/ij/).

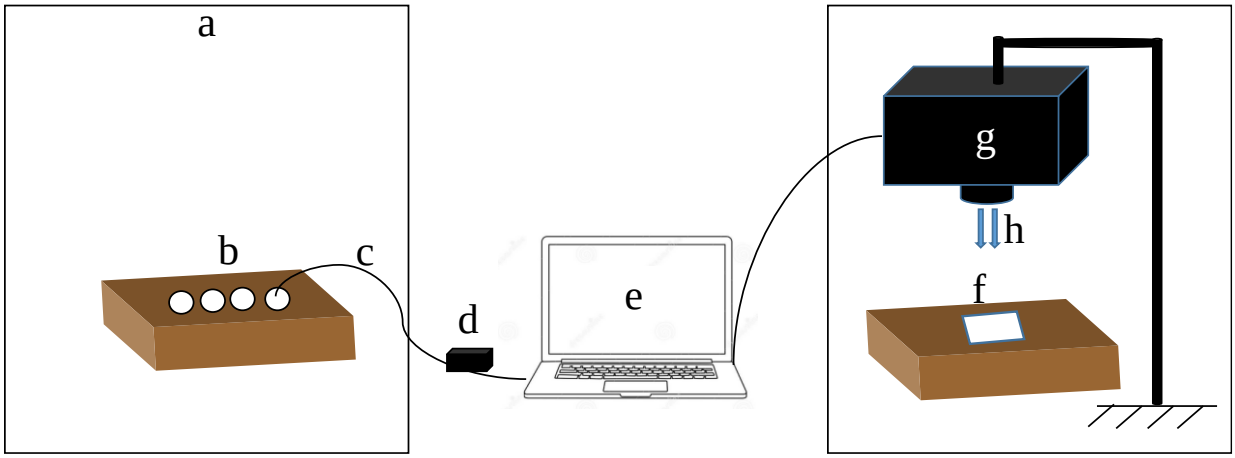


Figure II-6: Experimental set-up: a) dark room, b) petri dish containing soil+granule with spots deposited above, c) fiber optic cable, d) fiber optic pH meter, e) computer, f) petri dish containing soil+granule with optode deposited above, g) camera, h) excitation light (integrated in the camera)

For each treatment, three petri dishes were devoted for pH measurement with spots and one petri dish for planar optodes measurements. 156 self-adhesive spots (7 mm) were stuck in line onto clean glass slides (each 13 spots is designed for one petri dish * 3 petri dishes * 4 treatments). The spots were soaked at least 3 hours in a 100 Mm phosphate-buffered saline for equilibration and rinsed prior to be placed on the soil surface. Each glass slide was then placed on the soil surface by placing the central spot above the fertilizer granules, corresponding to the section S0 (S0= 0-7 mm = spot 1 with d=7 mm). The other spots were placed at different distances from the granule (**Figure II-7**): 7-14 mm (S1), 14-21 mm (S2), 21-28 mm (S3), 28-35 mm (S4), 42-49 mm (S5) and 56-63 mm (S6).

Planar optodes were cut into small (2 cm*1.5 cm) and large rectangles (6 cm*1.5 cm) and they were sticked to glass slides and equilibrated in a buffer solution as described previously for the spots. The glass slide with the large rectangular foil sensor was placed on the center of the petri dish above the fertilizer granule, and covering a soil surface of 9 cm^2 while the two small pieces of the planar optodes were placed in the petri dish borders and covering a surface of 6 cm^2 each. This configuration provides a spatial distribution of pH variation at a radius of 6 cm around the fertilizer granule **(Figure II-7)**.

The petri dishes were then sealed with parafilm to prevent moisture loss and covered with aluminum foil to protect optodes from ambient light. After that, the petri dishes were incubated for 28 days at 25°C in darkness. pH measurements were made in a custom-made dark chamber after 6 h, 1, 2, 3, 6, 7, 10, 15, 20, 24 and 28 days of incubation. The petri dish was closed again until the following measurement, with a moisture control and readjustment to 60% WHC. To this end, water was homogeneously added evenly through holes on all the four sides of the petri dish, thus avoiding interfering with the sensors and the P diffusion.

Calibration of the spots and planar optodes was carried out in phosphate (Na_2HPO_4 and NaH_2PO_4) buffer solution adjusted to an ionic strength (IS) of 20 mM. As fluorescent pH probes are sensitive to IS [148], the IS of the buffer solution was adjusted to 20 mM with NaCl. This IS is calculated based on the electric conductivity of the soil sampled at a radius of 20 mm around the TSP fertilizer and using the equation developed by Alva et al. [149].

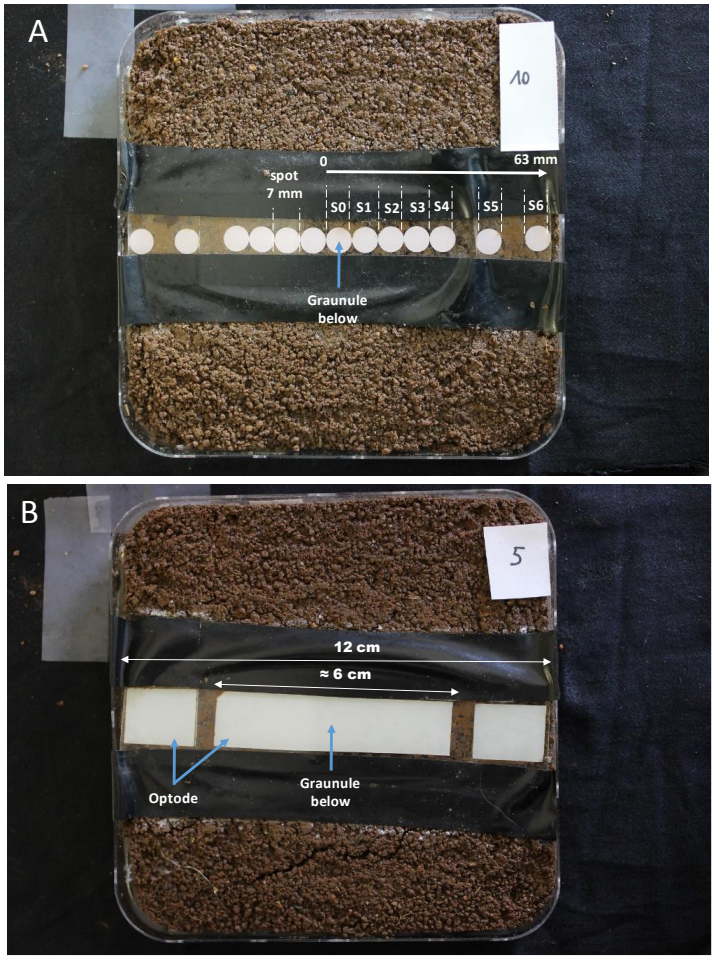


Figure II-7: petri dishes with soil and a TSP granule in the middle, with A) spots and B) optodes placed on glass slides and fixed to the soil surface

2.2.4. Measurements of different pools of P

After the last pH measurement at the 28th day of incubation, the soil was collected for P measurements. Small cylinders (d=7 mm, h=2 cm) were used to collect with precision the soil from the distances S0, S1, S2, S5 and S6 as described in the **Figure II-8**. For each point, except the center, the soil was sampled in the four directions from the center of the box by symmetry. A split of the soil samples was used for resin-P measurements and a second split for microbial P measurements. Resin-P targets the phosphate ions in solution and loosely sorbed onto soil surfaces, therefore it represents the plant available P [150]. Microbial-P expresses the P contained in soil microorganism cells and determined by fumigation-extraction [151].

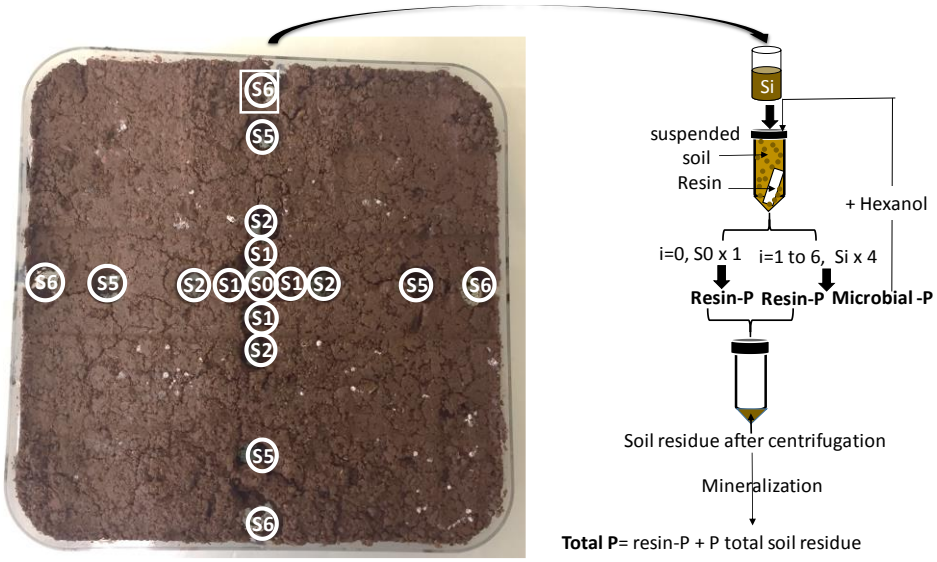


Figure II-8: Collection of soil at different distant from the granule after 28 days of incubation, to measure different forms of phosphorus

Sheets of anion exchange resins (AER) (6 cm*2 cm) were used to measure resin-P and microbial-P. For S0, the essay was downscaled in order to maintain the same liquid:solid:resin surface ratio. The measurements of resin-P and microbial-P were made following the protocol proposed by Kouno et al. [151]. Briefly, AER (reference: VWR 551642S) were first shaken 1 hour in 0.5 M $NaHCO_3$ using end-over-end shaker, and then washed with water. This operation was repeated twice. For resin-P, about 1 g of dried soil (0.5 g for S0) was weighed and 30 ml of distilled water was added as well as the resin strip and samples were shaken horizontally at least 16 hours. For microbial P, we followed the same method as for resin-P, except the addition of 1 ml of hexanol for fumigation before shaking step (cell lysis). The calculation of microbial-P was performed by the difference between the measured P from fumigated and unfumigated soil at each distance. The elution of the adsorbed P was made by shaking the AER in 30 ml of

0.1 M NaCl+HCl for 2 hours and the concentration of P was determined colorimetrically using the malachite green method [152].

The soil used to determine the resin-P was recovered by centrifugation to determine the remaining total P. The analysis of total soil phosphorus was done by transforming relatively insoluble forms of P into soluble forms that are compatible with colorimetric determination methods. For that, The soil (50 mg) was digested by microwave at 220 °C using 1 ml of 15.6 M nitric acid, and P concentration was determined using the colorimetric method with malachite green [152]. To determine the total P content at each distance, resin-P and total P remaining at each distance have been summed. This parameter was important to calculate the recovery of P fertilizer, using the **Equation 8** [121].

$$PfSi = \frac{([\mathrm{Pf}]\mathrm{Si} * \mathrm{Wi})}{\sum_i ([\mathrm{Pf}]\mathrm{Si} * \mathrm{Wi})} \qquad \textbf{Equation 8}$$

where, i is the soil section at different distance from the granule application (i=0, 1, 2, 3, 5, 6), [Pf]Si and Wi are the concentration of total P of Si (mg/kg) and the soil weight at each distance (kg), respectively. [Pf]Si is calculated by subtracting the P concentration of the unfertilized soil from the concentration of the fertilized soil.

3. Data analyses

The average values were calculated for each treatment. Analysis of variance (ANOVA), mixed models and correlation matrixes among treatments were performed using R version 3.4.2. One-way ANOVA was performed to study the effect of formulation on contact angle (CA), Young's modulus (EM), tensile strength (TS), elongation at break (EB), and thickness of the coating agent. Two-way ANOVA was performed to study the effect of fertilizers treatment and distance from fertilizers on resin-P, microbial-P, total P and P recovery. Correlation matrix was used to determine correlations between films and coated TSP characteristics. For mixed models (Package: lme4), they were performed to study the effect of formulation and time on P release in water with formulation and time as fixed effects and the bottle (containing fertilizer and water) as a random effect. The effect of coated fertilizers, distance from fertilizer and time (fixed effects) on soil pH was also investigated with petri dish as the random effect. If significant, Tukey's (for ANOVA) and Emmeans (for mixed models) post hoc tests were used for pairwise multiple comparisons ($p < 0.05$).

CHAPTER III. TSP coatings properties and phosphorus release: effects of biopolymer types and plasticizers addition

The objectives of this chapter are to (i) study the effect of the biopolymers types and plasticizers addition on the formulation properties of a new generation of coating based on lignin from olive pomace residue and polysaccharides/plasticizers and (ii) correlate the physicochemical properties of different composite formulations on the P release behavior in water. For this purpose, we used two strategies: (1) Preparation of composite films and characterization of their surface, mechanical, textural and thermal properties, (2) Coating of TSP granules using the same formulations than for the composite films and study of their water absorption, morphology and P release. This work has been valued in three published articles (in annexes):

"**Fertahi, S.**, Bertrand, I., Amjoud, M., Oukarroum, A., Arji, M. and Barakat, A., 2019, Properties of Coated Slow-Release Triple Superphosphate (TSP) Fertilizers Based on Lignin and Carrageenan Formulations, *ACS Sustainable Chemistry & Engineering*, 7, 10371−10382."

"**Fertahi, S.**, Bertrand, I., Ilsouk, M., I., Amjoud, M., Oukarroum, A., Zeroual, Y. and Barakat, A., 2020, New generation of controlled release phosphorus fertilizers based on biological macromolecules: Effect of formulation properties on phosphorus release, *International Journal of Biological Macromolecules*, 143, 153–162."

"**Fertahi, S.**, Bertrand, I., Ilsouk, M., I., Amjoud, M., Oukarroum, A., Zeroual, Y. and Barakat, A., 2020, Impact of plasticizers on lignin-carrageenan formulation properties and on phosphorus release from coated TSP fertilizer", *ACS Industrial Chemistry and Engineering Research*, 59, 31, 14172–14179."

1. Effect of biopolymer types on the coating formulations properties and on the phosphorus release behavior in water

1.1. Introduction

According to the literature, the coating materials applied most frequently are sulfur [33,34], waxes [153], polystyrene [154], polyethylene [153,155,156], poly(N-isopropylacrylamide) [157,158], polyurethane [157], polysulfone [46,47,84,159], polyacrylonitrile [46,47], etc. However, the combination of fertilizer and polymeric coatings has some disadvantages. The majority of synthetic polymers require organic solvents (e.g., N-dimethylformamide [47], chloroform [49]) for solubilization, which are harmful to the environment. In addition, the polymers remain in the soil when the nutrients are exhausted. According to Trenkel [26], the use of polymeric materials in coatings could lead to an undesirable accumulation of plastic residues of up to 50 kg/ha/year. The development of environmentally friendly CRFs using

biodegradable polymers derived from biomass, agricultural and agro-industrial waste (carbohydrates, lignin, etc.) is a much better solution. Compared to synthetic polymers, biological macromolecules are relatively inexpensive [52], biodegradable, nontoxic for soil organisms and contribute to the improvement of soil properties [53,54]. In addition, biological polymers appear to be a potential alternative to synthetic polymers for CRFs coatings and could contribute significantly to organic waste recycling and the circular economy. Lignin, mainly recovered as a byproduct from wood pulping processes, is a cheap and natural polymer available as a waste material with approximately 100 million tons produced annually worldwide [160]. Moreover, compared to other polymers, lignin is a renewable, biodegradable, relatively hydrophobic biopolymer that is rich in recalcitrant carbon, which could contribute to increasing the soil organic matter content [45]. Studies using commercial lignin blended with additives as a coating agent (rosins and linseed oil [16,45], alkenyl succinic anhydride [161]) showed its efficiency at decreasing the release rate of nutrients from fertilizers. Polysaccharides are also used in coating formulations. However, these compounds have never been tested alone. They are always mixed with other polymers or other components, such as clays [88]. Wan et al. [50] reported that k-carrageenan-Na-alginate and k-carrageenan-g-poly(acrylic acid)/celite composite superabsorbents were used as inner and outer coating materials, respectively, for nitrogen fertilizer. This double-coated fertilizer had slow-release behavior and improved the water-holding capacity and water-retention properties of the soil.

This part 1 presents results on the possibility of using lignin (LG) extracted from olive pomace (OP) biomass and some commercial polysaccharides (alginates (AL) from brown algae, carrageenan (CR) from red algae and carboxymethyl cellulose (CM) from wood pulp) for the preparation of TSP fertilizer coatings. The choice of these polysaccharides is based on the availability of their basic materials (algae and wood), their ability to form stable and homogenous formulations for TSP coatings and their high water absorption capacity [50]. The main objective of this chapter is to evaluate the influence of different biopolymers coatings on the P release behavior of coated granules.

1.2.Characterization of olive pomace (OP) and lignin

Compared to wood and other lignocellulosic biomass, olive pomace (OP) is rich in lignin (LG) (33.2% ± 2.22a) [162], while its contents of hemicellulose, cellulose and ash were estimated to be (10.29% ± 0.02b), (14.8% ± 0.43b) and (4.95%), respectively. The elementary composition of OP biomass (**Table III-1**) was estimated to be 51% C, and the C/N ratio was 71.85. The

alkali-extracted OP lignin contained more C, H, N and S than the raw material and was comparable to alkali-extracted lignin from Masson's pine sulfate pulping liquor [163].

Table III-1: Chemical analysis of olive pomace (OP) and extracted lignin (LG) (n =2)

	C %	H %	N %	S %	O%
OP	51.02 ± 0.11[a]	6.85 ± 0.14[a]	0.71± 0[a]	0.08 ± 0[a]	36.38 ± 0.25[a]
LG	58.24 ± 0.00[b]	7.89±0.03[a]	1.79 ± 0.01[b]	0.18 ± 0.01[a]	28.05 ± 0.07[b]

Within a column, means followed by the same letter are not significantly different at $p<0.05$

FTIR spectrum (**Figure III-1**) shows two intense bands at 2925 cm^{-1} and 2840 cm^{-1} related to the C–H stretching vibrations in aliphatic structures and to the symmetrical CH stretching vibrations in $–CH_2$, respectively, both of which are attributed to fatty acids [164]. The identified bands at 1610, 1515 and 1460 cm^{-1} correspond to aromatic ring vibrations, and the bands at 1705 and 1650 cm^{-1} can be attributed to nonconjugated and conjugated carbonyl groups, respectively [165]. Lignin-guaiacyl was identified at 1270 cm^{-1}, and lignin-syringyl was identified at 1370 cm^{-1}. The extracted OP lignin showed a typical FTIR spectra of guaiacyl-syringyl lignin in agreement with Xiao-Xia [163] and Gutierrez [165].

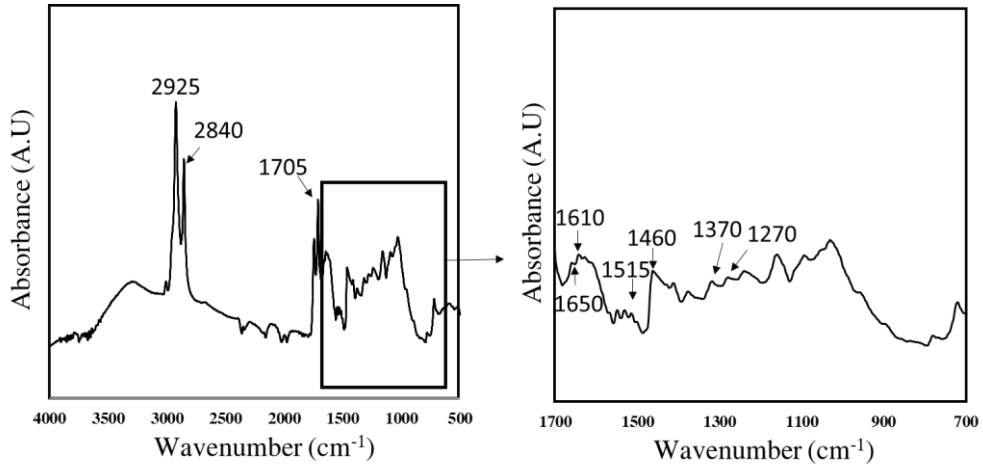


Figure III-1: FTIR spectra of alkali lignin (LG) extracted from OP

1.3.Characterization of lignin-polysaccharide composite formulations

1.3.1. Surface properties of composite films

The hydrophobic behavior of coatings is required to minimize water penetration inside the fertilizer core and its rapid dissolution. A significant difference in contact angle was observed between different formulations (p-value < 0.05) **(Fig III-2)**. The hydrophobicity of formulation composites decreased in the following order: CM = CR > > LGCM = LGAL = LGCR> AL= LG. No significant difference was observed between CM (98°) and CR (98°) films, which are more hydrophobic than alginate and lignin composite films with contact angles of 57° and 53°,

respectively. The low contact angle of the lignin film could be attributed to the presence of HO^- Na^+ groups in lignin (after solubilization in NaOH).

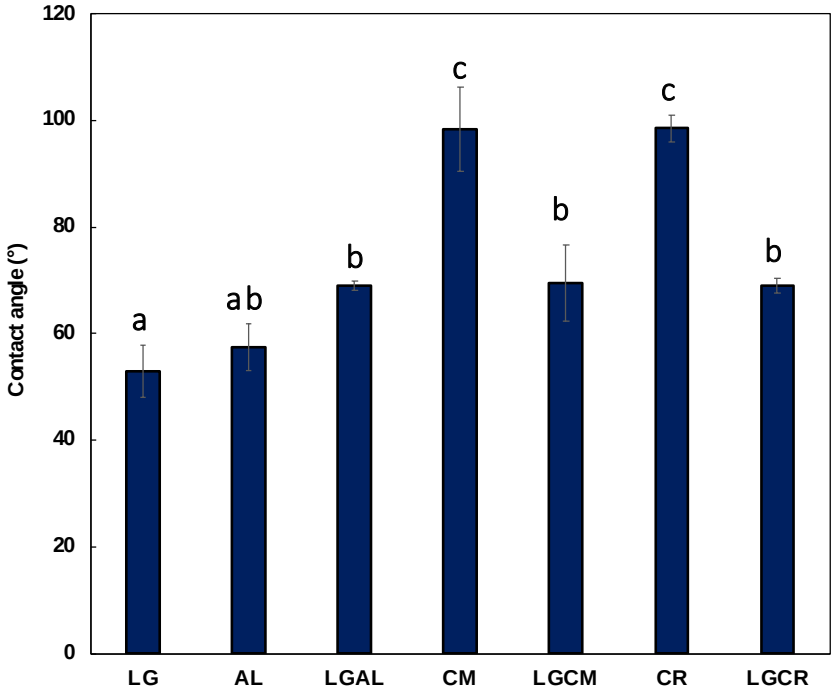


Figure III-2: Contact angle of composite films, LG: lignin, AL: alginate, CM: carboxymethyl cellulose, CR: carrageenan, LGAL: lignin-alginate, LGCM: lignin- carboxymethyl cellulose, LGCR: lignin-carrageenan. Different letters indicate significant differences ($p<0.05$)

Notley and al. [166] reported that the contact angles of softwood kraft lignin and softwood milled wood film (thickness: 50-60 nm) were 46, 52.5 and 55.5°, respectively. Norgren [167] also reported that softwood lignin films with a thickness of 20-140 nm had a contact angle of 46°, which is in good agreement with our study. In another study, Ramirez et al. [168] reported that the contact angle of CM was estimated to be 83, compared to 98° obtained for CM in this work. This difference could be due to the difference in the total solid content, the thickness of the CM composite film and the surface roughness. Lijun Yang et al. [169] obtained for alginate film a contact angle of approximately 59° compared to 53° obtained in this study. They attributed this value to the hydrophilic surface of this material due to hydrophilic hydroxyl functional groups in the AL polymer. The contact angle obtained for CR was 98° in agreement with the CA values of iota-carrageenan ranged between 88.3°-115.2° as reported by Karbowiak et al. [141]. The authors attributed this hydrophobic behavior of the iota-CR film to the three-dimensional helical structure of the carrageenan polymer, with strong intramolecular hydrogen bonding beneath the film surface and no orientation of polar groups at the surface. Jayasekara

et al. [170] also observed this phenomenon with starch composite film. We also noticed that the addition of lignin (LG) to the polysaccharide formulation with a mass ratio of 4/1 (LG/polysaccharides) modified the hydrophobicity of the composite formulations (**Figure III-2**). The presence of lignin in the formulation tends to decrease the surface hydrophobicity of lignin-polysaccharide composites. Shankar et al. [171] found the same phenomenon. They reported that the contact angle of agar-lignin films was lower than that of agar films, and this reduction in contact angle might be due to the high roughness of the film after the addition of lignin.

1.3.2. Mechanical properties

Figure III-3 shows the typical stress-strain curves of different composite films. The elastic modulus (EM), tensile strength (TS) and elongation at break (EB) depend on the type and structure of the polysaccharides in the composites (p-value < 0.05) (**Table III-2**). The EM, TS and EB of the obtained composite films varied between 225-1191 kPa, 1135-3674 kPa and 1.5 - 44%, respectively. The tensile strength of the lignin (LG) film was 1135.09 ± 766 kPa, which is lower than that of the polysaccharide-incorporated composite films (**Table III-2**). Aadil et al. [141] reported that the tensile strength of lignin films extracted from acacia wood and blended with alginate was 413 ± 2 kPa, while the tensile strength increased to 625, 569 and 466 kPa with the addition of the different plasticizers, glycerol, epichlorohydrin and PEG 4000, respectively. Lignin extracted from OP (this study) has a greater tensile strength than acacia wood lignin, even when blended with alginate and plasticizers. This is probably due to the presence of fatty acids in lignin from OP (discussed in the section 1.2). Fatty acids are usually used as plasticizers in composite formulations [172], and their presence can play a role in natural plasticizers in different lignin formulations. The lignin-carrageenan (LGCR) composite exhibited higher elastic modulus (1191 kPa) and tensile strength (3674 kPa) than the LGAL and LGCM composite films. It is also of interest to note that tensile strength and elongation at break were significantly increased by 224% and 542%, respectively, with the addition of CR compared to LG, while the addition of CM significantly increased the elongation at break by 2910%. This increase in elongation at break compared to LG film can be explained by the hygroscopicity of polysaccharides. These compounds are more hygroscopic than LG polymers; hence, water uptake could explain the plasticization behavior [173]. However, in the case of lignin loaded with alginate, no strong effect on mechanical properties was observed compared to the LG film. The lignin polymer is known by its tridimensional and porous surface structure that might aid in compatibility with the polysaccharides. These phenomena have also been observed in the plant cell wall, confirming the lignin-polysaccharide interaction [174,175]. It is

noteworthy that films with high elasticity and tensile strength are good candidates for fertilizers coating and for a good control of P release.

Table III-2: Tensile modulus (EM), tensile strength (TS) and elongation at break (EB) of composite films. LG: lignin, LGAL: lignin-alginate, LGCM: lignin-carboxymethyl cellulose, LGCR: Lignin-carrageenan, n=3

Formulation	EM (kPa)	TS (kPa)	EB (%)
LG	786,93 ± 385^{ab}	1135.09 ± 766^{a}	1.46 ± 0.11^{a}
LGCR	1191,51 ± 356^{a}	3674.11 ± 318^{b}	9.37 ± 1.99^{b}
LGCM	225.49 ± 96^{b}	2510.98 ± 754^{ab}	43.94 ± 15.99^{c}
LGAL	612.53 ± 65^{ab}	1653.57 ± 261^{a}	2.79 ± 0.43^{a}

Within a column, means followed by the same letter are not significantly different

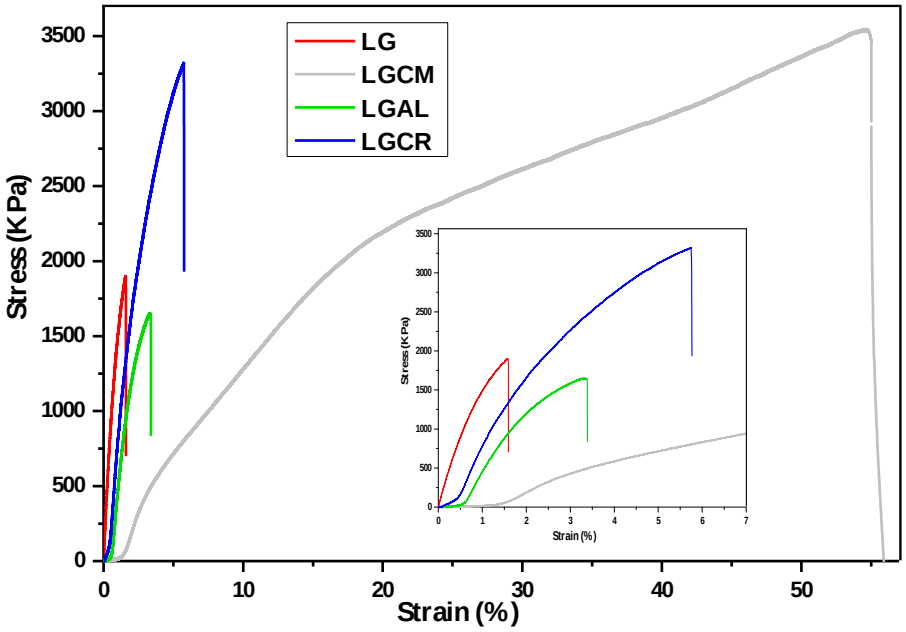


Figure III-3: Typical stress-strain curves of film composites: LG: lignin, AL: alginate, CM: carboxymethyl cellulose, CR: carrageenan, LGAL: lignin-alginate, LGCM: lignin-carboxymethyl cellulose, LGCR: lignin-carrageenan, n=3

1.3.3. Thermogravimetric analysis

The thermal stability and degradation behavior of polysaccharides and lignin-polysaccharide composites were assessed using TGA and weight loss curves. **Figure III-4A** presents the TGA analysis of the polysaccharide films. From these curves, we can observe that the thermal degradation of all polysaccharides occurs in three steps. The first step at 25-105 °C corresponds to water desorption, with approximately 9-13% overall weight loss due to dehydration. The second decomposition stage starts at 192°C for the AL and CR films and 230°C for the CM film. This step is attributed to the thermal degradation of polysaccharides. In the last step, the

AL and CM films lost approximately 50% of their weight at 340°C, while the CR film had to reach 422°C to lose the same percentage of weight. This mass loss is related to the formation of byproducts of polysaccharides during the thermal degradation process [176]. Based on the TGA analysis (**Figure III-4B**) of LG and composite films, the lignin film had fast thermal degradation compared to the lignin-polysaccharide blended film. The thermal behavior of the LGAL and LGCM composites seemed to be similar. These films exhibited the slowest thermal degradation, followed by the LGCR and LG films. The 50% weights of LG and LGCR were lost at 450°C and 454°C, respectively, while LGCM and LGAL lost 50% of their initial mass at 464°C.

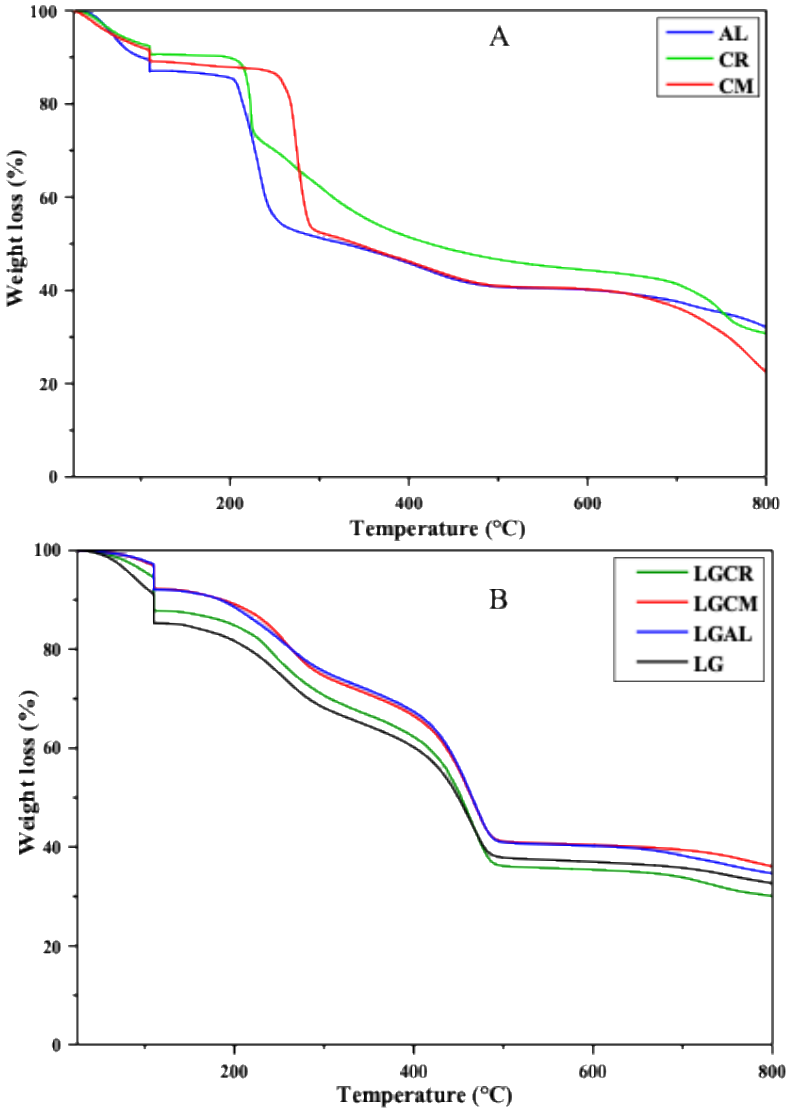


Figure III-4: TGA of (A) polysaccharide films (AL: alginate, CM: carboxymethyl cellulose, CR: carrageenan) and (B) LG and composite films (LG: lignin, LGAL: lignin-alginate, LGCM: lignin- carboxymethyl cellulose, LGCR: lignin-carrageenan)

The blending of lignin with polysaccharides enhanced the thermal stability of the three materials. LG, CM and CR films underwent the active weight loss step at 25-290 °C, while this

step occurred at 25-500°C with the addition of lignin. In general, the mass loss of composite-polymer films occurred between 25 and 500°C [177,178]. Changhua Liu [177] reported similar intervals of degradation temperatures of lignin-poly (4-vinylpyridine) films.

1.4.Characterization of coated TSP fertilizer properties

1.4.1. Morphological characterization of coated TSP fertilizers

Figure III-5 presents images of coated TSP. Morphological features of TSP granules and coatings were observed using SEM (**Figure III-6)**. The visual aspect of the polysaccharides-coated TSP fertilizer was similar to that of uncoated TSP (polysaccharides solution was colorless), while the granules coated by lignin-based formulations were brown. The average thickness of the layers (TSP/polymer ratio of 15/1 (wt/wt)) evaluated by SEM, was 71.3±23.6μm. The coating formulation has no significant effect on coating thickness (p-value > 0.05).

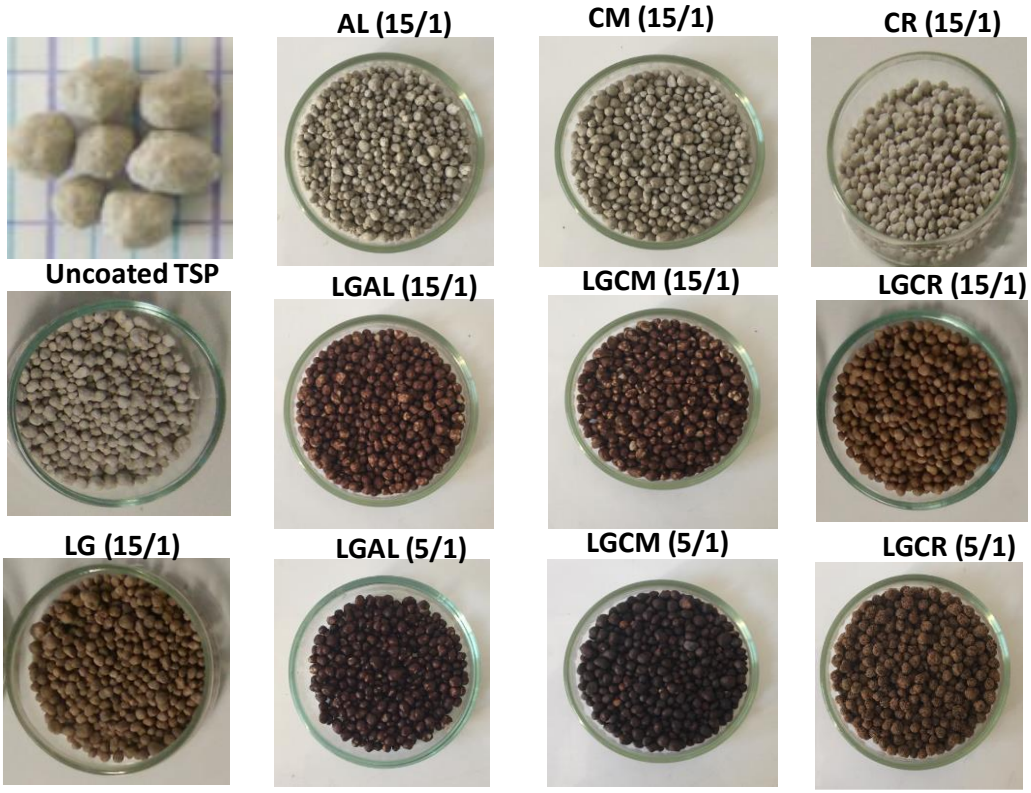


Figure III-5: Real image of noncoated TSP and coated TSP at the TSP/polymer ratio of 15/1 with LG (lignin), AL (alginate), CM (carboxylmethyl cellulose), CR (carrageenan), LGAL, LGCM and LGCR, and at the TSP/polymer ratio of 5/1 with LGAL, LGC and LGCR

The coating thickness is an important parameter that can control the nutrient release rate [20,47]. The effect of two ratios of TSP/polymers (15/1 and 5/1 (wt/wt)) on the coating agent thickness was studied, and the results are shown in **Figure III-7**. A significant effect on coating

agent thickness was observed between ratios for the granules coated with the three formulations. The coatings formed with a higher polymer concentration exhibited higher thickness (135.6±20.9µm) for the TSP/polymer ratio of 5/1 than the 71.3±23.6 µm observed for the TSP/polymer ratio of 15/1. This result is in agreement with the previous report of Jarosiewicz et al. [47], suggesting an increase in the thickness with increasing polymer concentration in the coating solution.

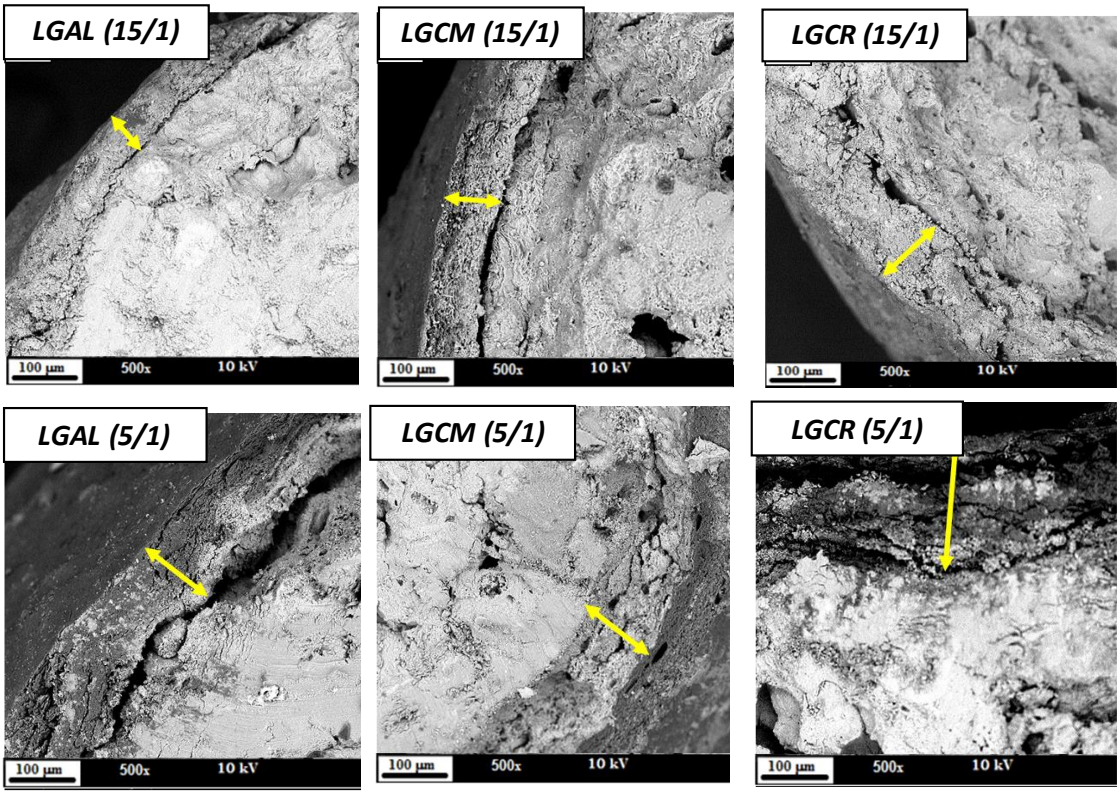


Figure III-6: SEM of cross-section of the coated TSP fertilizer at the TSP/polymer mass ratios of 15/1and 5/1 with LGAL (lignin-alginate) LGCM (lignin- carboxymethyl cellulose) and LGCR (lignin-carrageenan)

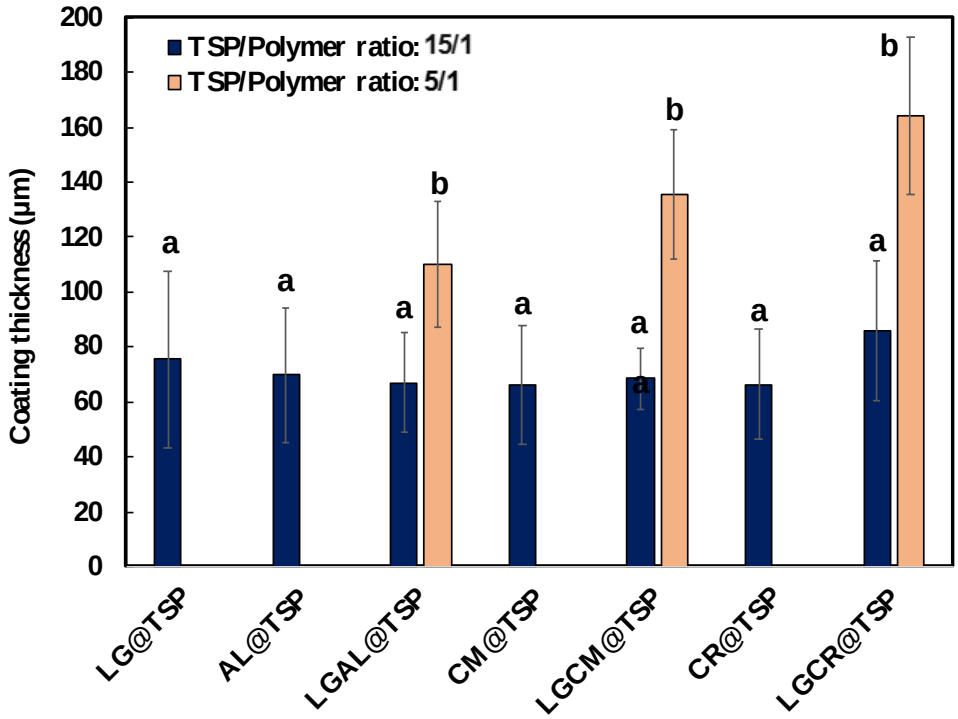


Figure III-7: Thickness of coating layers on TSP granules coated with LG (lignin), AL (alginate, LGAL (lignin-alginate), CM (carboxylmethyl cellulose), LGCM (lignin-carboxylmethyl cellulose), CR (carrageenan) and LGCR (lignin-carrageenan). Different letters between treatments indicate significant differences ($P<0.05$, $n=9$).

1.4.2. Hygroscopicity

Figure III-8 illustrates the water absorption of uncoated and coated TSP within 3 days at different levels of relative humidity (RHs) (35%, 60% and 80%). The water absorption of all formulations coatings increased with increasing air humidity and with time. LGCR@TSP, LGAL@TSP and LGCM@TSP exhibited the highest hygroscopicity in the following order: LGCR@TSP > LGAL@TSP > LGCM@TSP. According to Liang et al. [125], the water absorption of coating polymers depends on many factors, such as the amount of hydrophilic groups and elasticity of the polymer networks and layers' porosity. As previously mentioned in **Table III-2**, LGCR exhibited the highest elastic modulus (1191.51±356 kPa), followed by LGAL (612.53 ± 65 kPa) and then LGCM (225.49±96 kPa). The major result was that the water absorption of the coating increased when the elasticity increased, which could improve the swelling properties of the coated fertilizers. It is noteworthy that a coated fertilizer with swelling and slow release behavior could effectively improve the utilization of both fertilizer and water resources [125].

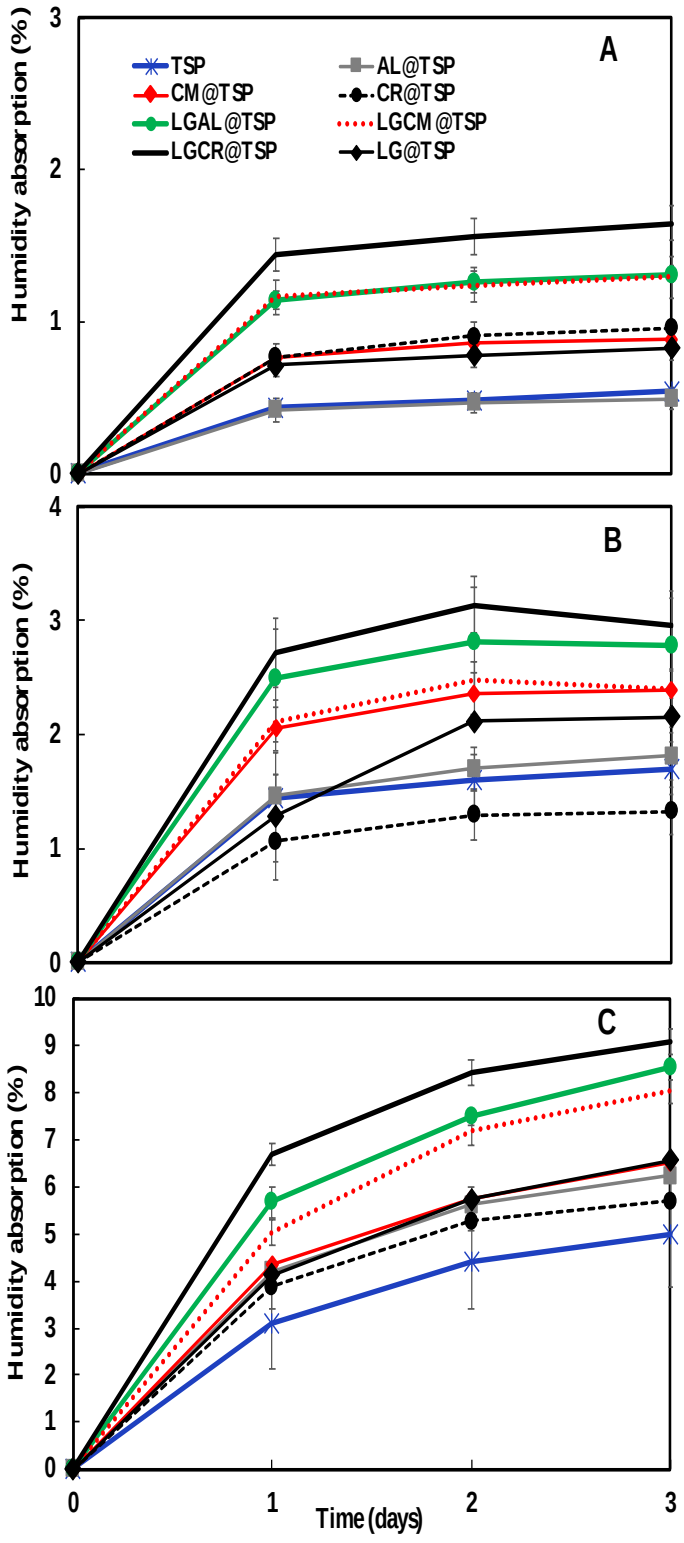


Figure III-8: Water absorption (WA) of uncoated and coated fertilizers over time at different relative humidities: (A) 35%, (B) 60% and (C) 80% RH with LG (lignin), AL (alginate), CM (carboxylmethyl cellulose, CR (carrageenan) LGAL (lignin-alginate), (G) LGCM (lignin-carboxylmethyl cellulose) and LGCR (lignin-carrageenan), n=3

1.5.Release behavior of phosphorus from coated TSP fertilizers

As shown in **Table III-3**, the uncoated TSP released approximately 72±0.4, 85±140 and 99.5±4.3% of P in distillated water within 6, 24, and 72 h, respectively. In contrast, the fertilizers coated with only lignin or only polysaccharides or with both lignin-polysaccharides (the TSP/polymer ratio of 15/1) released P in the range of 19.3-55.7% (**Table III-3**) within 6 h, 52-77.1% within 24 h and 68.3-80.6% within 72 h, which are slower that uncoated TSP. The slowest P release was observed with the LGCR@TSP formulation within the first and second days.

Table III-3: Release behavior of TSP and coated TSP with different polymers in water, TSP coated with LG: lignin, AL: alginate, CM: carboxymethyl cellulose, CR: carrageenan, LGAL: lignin-alginate, LGCM: lignin- carboxymethyl cellulose, LGCR: lignin-carrageenan, n=3

Formulation	TSP/ Polymer ratio	P-release in water (%) over time (h)					
		6	24	48	72	96	120
TSP	-	72.0 ± 0.4^{a}	85.0 ± 14^{a}	95.0 ± 2.7^{a}	99.5 ± 4.3^{a}	-	-
LG@TSP	15/1	34.3 ±4^{ab}	55.5±6.4^{a}	64.1±1^{bc}	65±9.8^{bcd}	71.6± 1.8^{abcd}	76±0.7^{a}
CR@TSP	15/1	44.9 ± 4.9^{ab}	60.9 ± 0.7^{a}	69.5 ± 7.8^{ab}	78.1 ± 5.7^{abcd}	84.7 ± 15^{a}	90.2 ± 3.8^{b}
CM@TSP	15/1	39.7 ± 7.6^{ab}	77.1 ± 0.1^{a}	73.8 ± 4.7^{bc}	79.5 ± 3.5^{abc}	75.1 ± 1.7^{abc}	73.7 ± 1.1^{a}
AL@TSP	15/1	19.3 ± 13^{b}	76.7 ± 0.1^{a}	77.9 ± 6.6^{abc}	80.6 ± 10^{ac}	77.3 ± 5.5^{ac}	75.3 ± 4.4^{a}
LGCR@TSP	15/1	28.2 ± 4.8^{ab}	52.0 ± 6.5^{a}	59.0 ± 8.9^{abc}	72.5 ± 1.2^{abcd}	78.8 ± 2.0^{abcd}	75.3 ± 4.0^{abcd}
LGCM@TSP	15/1	55.7 ± 9.4^{ab}	66.7 ± 0.8^{a}	73.1 ± 4.8^{bc}	71.9 ± 0.5^{bcd}	69.6 ± 0.9^{abcd}	68.5 ± 1.1^{ad}
LGAL@TSP	15/1	51.7 ± 9.9^{ab}	74.5 ± 0.1^{a}	67.1 ± 1.7^{bc}	68.3 ± 3.1^{bcd}	68.7 ± 3.1^{abcd}	64.9 ± 0.5^{acd}
LGCR@TSP	5/1	-	59.1 ± 1.9^{a}	60.0 ± 1.0^{c}	59.5 ± 1.9^{bd}	60.4 ± 3.0^{bcd}	59.3 ± 1.6^{cd}
LGCM@TSP	5/1	-	59.9 ± 1.8^{a}	59.0 ± 1.4^{c}	58.9 ± 2.4^{d}	57.4 ± 0.8^{bd}	59.2 ± 2.2^{cd}
LGAL@TSP	5/1	-	56.3 ± 3.3^{a}	61.7 ± 3.9^{bc}	57.9 ± 5.5^{d}	55.1 ± 3.7^{d}	55.8 ± 3.5^{c}

Within a column, means followed by the same letter are not significantly different

The release behaviors of TSP coated with LGCR, LGCM and LGAL formulations at TSP/biopolymer ratios of 15/1 and 5/1 are shown in **Table III.3** and a significant effect of TSP/biopolymer ratios (the effect of coating thickness) on the release response from LGAL@TSP and LGCM@TSP (p-value<0.05) was reported, but not LGCR@TSP. As previously presented in **Figure III-7,** the TSP/biopolymer ratio (5:1) resulted in a high thickness. A higher polymer coating concentration decreased the P release of coated TSP granules due to the increase in coating layer thickness. After 3 days, TSP coated with LGCR, LGCM and LGAL formulations at the TSP/biopolymer ratio of 15/1 (thickness=71.3±23.6μm) released 72.5%, 71.9% and 68.3% of P, respectively, while TSP coated with the same formulations using a TSP/biopolymer ratio of 5/1 (thickness=135.6±20.9μm) released only 59.5, 58.9 and 57.9% of P . These results are in agreement with other studies in the literature.

Lubkowski et al. [62] showed that the release of phosphate from uncoated fertilizer was very fast and that all phosphates were released within 50 min, while coated NPK with different thicknesses (0.047–0.5425 mm) revealed a smaller release of phosphate in comparison with the initial NPK. Jarosiewicz et al. [47] showed that the release rate of NPK can be controlled by adjusting the thickness of the coating. They argued that NPK granules with double or triple-layered coatings (high thickness) released nutrients much slower than granules coated with one layer. NPK granules coated with one layer of 17% polyacrylonitrile (thickness ≈ 0.2 mm) released 93.7% of K^+ within 5 h, while granules with three layers of the same formulation (thickness ≈ 0.49 mm) released only 11.7%. Behin et al. [179] confirmed that the release of nitrogen depends strongly on the thickness of the coating. They reported that the dissolution rate decreases with increasing coating percentage. For urea coated with acetylated kraft lignin and sulfite lignin, dissolution rates of 88 and 97%, respectively, were obtained after 24 h for the sample with a 5.0% coating, whereas only 43 and 72% were obtained for the sample with a 15.0% coating.

Table III-4 provides a comparative study of the results obtained in this part 1 and those from previous studies using lignin as a coating material. According to Perez et al. [64] that using lignin alone does not improve the delayed release of urea in water, which can be explained by the presence of the polar groups on its surface and the resulting good affinity with water. Mulder et al. [161] also employed lignin coupled with plasticizers and some other hydrophobic compounds and reported that complete nitrogen release through these coating materials still occurred within 1 h. To improve its coating properties, lignin has also been mixed with rosins as a coating system for soluble fertilizers such as phosphate fertilizer [16]. According to Garcia et al. [16], only 20% of P was released with this method. In comparison with these previous works, it can be concluded that our study is interesting in that we used low-cost materials based on OP, which can potentially be a good candidate for coating fertilizers and slowing the release rate of nutrients; however, our materials remain less efficient in this regard than synthetic polymers.

Table III-4: Comparative studies of different works using lignin as a coating material to control nutrient release

Coating materials	Fertilizer	Granule size (mm)	T drying (°C)	Coating methods	Thickness (μm)	Release rate (%)		Reference
Lignin + Polysaccharides	TSP	2-3	65	Rotating pan	77-211	Noncoated Coated	100% after 3 days 57-58% after 3days	This work
Commercial lignin + rosins	TSP	2		Rotating pan	83-106	Noncoated Coated	80% after 3days 20% after 3 days	Garcıa et al. [16]
Commercial lignins + plasticizers + hydrophobic compounds	Urea	-	70	Rotating pan	-	Noncoated Coated	>80% after 30min 60-80%after 30min	Mulder et al. [161]
Commercial lignin	Urea	0.5-5	-	Matrix	-	Non-treated Matrix	100% after <5hours 40-90% after 1hour	Perez et al. [64]

1.6. Correlations between P release behavior and physicochemical properties of coating films

To understand the relationship between P release behavior and physicochemical properties of film composites of coated TSP discussed previously in this part 1, a correlation matrix was constructed **(Table III-5)**. P release is strongly negatively correlated with elastic modulus (r= -0.81, *p=0.014*, while it is strongly positively correlated with elongation at break (r=0.93, *p=0.0008*). The young modulus represents the elastic deformation. When the coating material is elastic, the shell is able to resist the internal pressure created inside the core upon contact with water, and the P is released slowly without the shell being destroyed. A moderately negative correlation between P release and contact angle was also revealed (r= -0.49, *p=0.22*). This phenomenon could be explained by the fact that, when the contact angle is large, the coating material is hydrophobic, and then the affinity between the layer and water is weak. This lack of affinity prevents the penetration of large quantities of water inside the fertilizer core and then decreases the dissolution of TSP. For tensile strength and water absorption, a weak or no correlation was observed with P release (r<0.11, *p>0.78*). From these data and the discussion, we concluded that the LGCR formulation is the most efficient coating for mineral fertilizer due to its high elastic modulus, high CA, high water absorption and, as a consequence, slow release of P.

Table III-5: Correlation matrix between the properties of composite films and the coated TSP. Film properties: EM (elastic modulus), TS (tensile strength), EB (elongation at break) and CA (contact angle).

	P- Release	EB	EM	CA	TS	WA
P-Release	1					
EB	**0.93*** **	1				
EM	**-0.81***	**-0.71***	1			
CA	-0.49	-0.15	0.34	1		
TS	0.05	0.35	0.37	0.5	1	
WA	-0.11	0.25	0.26	**0.85****	**0.87****	1

p-value for correlations significance: (***) < 0.001; (**) < 0.01; (*) < 0.05.

2. Effect of plasticizer types on the coatings properties and on the phosphorus release behavior in water

2.1. Introduction

In most polymeric coating formulations, plasticizers are added to enhance film-forming polymer flexibility and to improve the mechanical properties of the coating shell [21,22,61,62,161]. Glycerol (GL) is one of the most commonly used plasticizers due to its high plasticizing capacity and thermal stability. It is relatively safe and biodegradable and is used as a food additive [180]. Many studies have shown that glycerol is used to improve the flexibility of films based on vegetal derived-biomass[181,182]. Polyethylene glycol (PEG) is a less hydrophilic plasticizer than glycerol. It is known to be a nontoxic, biocompatible, non-immunogenic, non-antigenic and biodegradable plasticizer [183]. Qussi et al. [184] showed that the addition of PEG increased the elongation at break of free shellac films. Nekhamanurak [185] and Yuan [186] also reported an increase in the elongation at break of poly(lactic acid)-$CaCO_3$ nanocomposites and cellulose acetate films respectively, plasticized by PEG.

From the first part, we concluded that lignin-carrageenan (LGCR) formulation is the most efficient coating for mineral fertilizer due to its good mechanical properties (highest elasticity and tensile strength), highest hydrophobicity and the slowest P release within the first days, compared to the other lignin-polysaccharides formulations. To the best of our knowledge, the effect of different plasticizer types and molecular weights on the properties of lignin-carrageenan blend films have not been reported thus far. We hypothesized that the addition of plasticizers would further improve the elasticity and plasticity of the LGCR coating materials. Therefore, in the present part, a series of films based on lignin extracted from olive pomace and carrageenan in the presence of three plasticizers (glycerol (GL), PEG 200 and PEG 2000) were prepared using a solution-casting method. The resulting blended films were evaluated for their

structure, morphology, thermal behavior, surface and mechanical properties and water absorption. The impact of plasticizer addition on P-release from different coating formulations was also evaluated.

2.2.Characterization of lignin-carrageenan-plasticizers composites

2.2.1. Structural FT-IR analysis

FTIR spectroscopy was used to eventually identify specific interactions between the lignin, carrageenan and plasticizers. **Figure III-9** shows the FTIR spectra of lignin, carrageenan, glycerol, PEG 200, PEG 2000 and composites in the range of 500-4000 cm^{-1}.

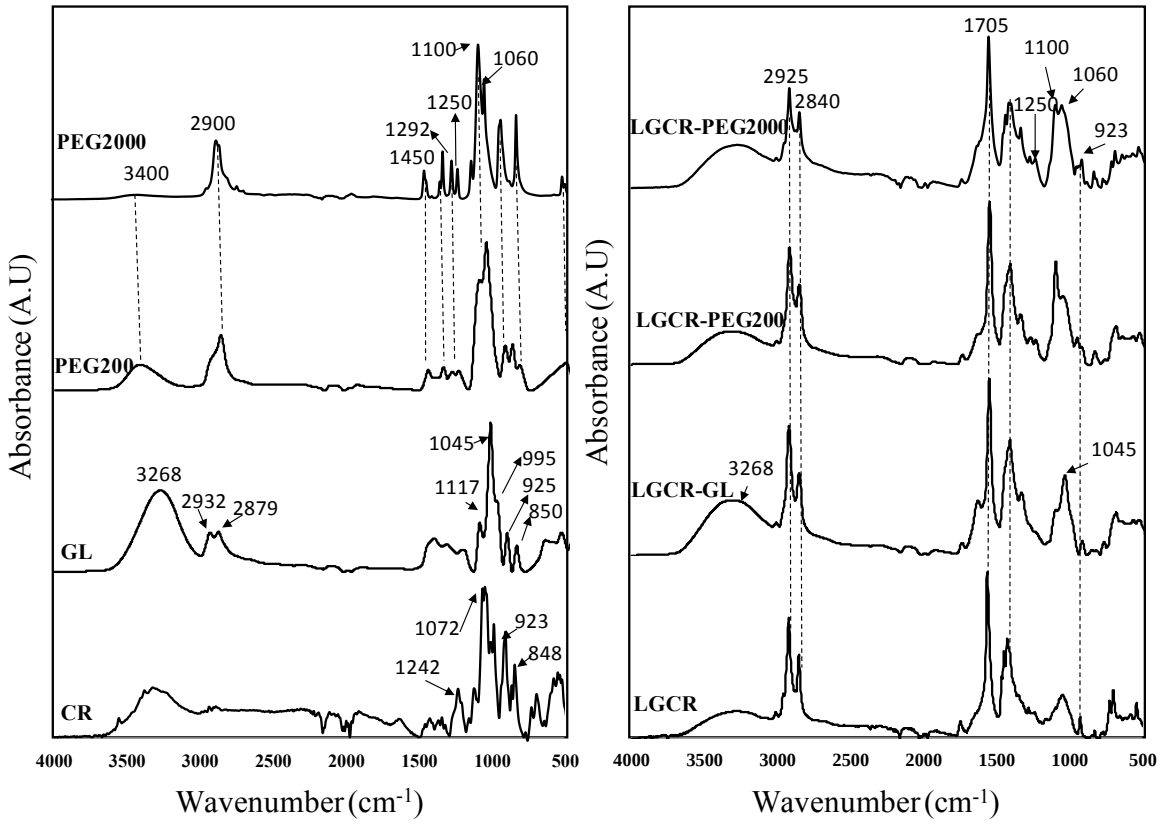


Figure III-9: FTIR spectra of k-carrageenan powder (CR), liquid glycerol (GL), liquid PEG 200, powder PEG 2000, LGCR film, LGCR-GL film, LGCR-PEG 200 film and LGCR-PEG 200 film.

Figure III-9A presents the IR spectrum of k-carrageenan powder. The characteristic band of sulfate esters (S=O) is assigned to absorption band at 1242 cm^{-1}. The adsorption bands at 1072 and 923 cm^{-1} correspond to the presence of the C_3-O-C_6 bridge of 3,6-anhydrogalactose and the band at approximately 848 cm^{-1} indicates the presence of C-O-SO_3 on C_4 of galactose [187–189]. FTIR spectrum of several major absorption bands representing the typical structure of lignin are shown in **Figure III-9B** and discussed previously in the first part, section 1.2. The spectrum of pure glycerol **(Figure III-9C)** shows several bands; C-H stretching vibration give

rise to two bands at 2932 cm^{-1} and 2879 cm^{-1} [190]. The bands observed at 850 cm^{-1}, and 995 cm^{-1} can be attributed to the vibrations of the skeleton C–C bonds. The bands at 1045 cm^{-1} and 1117 cm^{-1} correspond to stretching of the C–O linkage and to stretching of C–O, respectively [191]. The band at 3268 cm^{-1} is attributed to O-H stretching vibrations and the band at 925 cm^{-1} is ascribed to C-O-H stretching vibrations [192]. The FTIR spectra of PEG 200 and PEG 2000 (**Figure III-9D-E**) show several specific peaks: the band at 3400 cm^{-1} is attributed to O-H stretching of the hydroxyl group, and the peak at 2900 cm^{-1} corresponds to C-H stretching of the alkyl chain of the polymer. The peak at 1450-1292 cm^{-1} corresponds to C-H scissoring and bending, the peak at 1250 cm^{-1} corresponds to C-O stretching of the alcohol group, and the peak at 1100-1060 cm^{-1} due to the C-O-C ether group [193]. For LGCR, LGCR-GL and LGCR-PEG (200-2000) composite films, as expected, characteristic bands of lignin (2925, 2840, 1705 cm^{-1}), carrageenan (923 cm^{-1}), glycerol (3268, 1045 cm^{-1}) and PEG (1060, 1100, 1250 cm^{-1}) were all identified (**Figure III-9F-I**). The intensity of the band observed at 3268 cm^{-1} attributed to O-H stretching tends to increase with the addition of plasticizers

2.2.2. Morphological characterization

The micrographs (**Figure III-10**) reveal no difference between LGCR films with or without the plasticizers. Nevertheless, the LGCR-GL formulation showed a slight additional layer on the surface that may be associated with the glycerol plasticizer and could produce a less porous surface [66]. The thickness of the different films prepared was 241±43 μm.

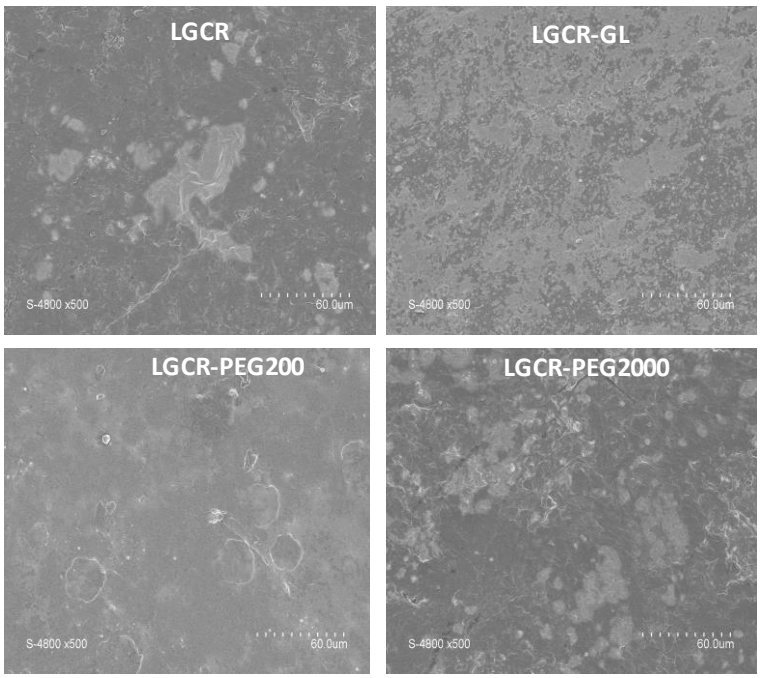


Figure III-10: SEM of composite films: lignin and carrageenan (LGCR)/glycerol (LGCR-GL), PEG 200 (LGCR-PEG 200), PEG 2000 (LGCR-PEG 2000)

2.2.3. Surface properties

Contact angle measurements were performed to investigate the surface properties and the effect of plasticizer type on the hydrophobicity of lignin/carrageenan composites. The structure and composition of the film surface could be affected by the addition of plasticizer [141]. The results showed that plasticized films exhibited significantly lower contact angles for LGCR-PEG 200 and LGCR-PEG2000 than LGCR films without a plasticizer. The contact angle of the LGCR/plasticizers (55% (w/w) LG, 15% (w/w) CR, 30% (w/w) plasticizer) films (at humidity and ambient temperature without prior equilibration) ranged between 36.1 and 64.32° and decreased in the following order of LGCR ≥ LGCR-GL > LGCR-PEG 2000 ≥ LGCR-PEG 200 (**Figure III-11**). The slight decrease of contact angle for LGCR in the presence of glycerol could be associated to the hydrophilic behavior of glycerol containing hydroxyl groups that have the ability to establish hydrogen bonds with water. This result is in accordance with Karbowiak et al. [141] who reported that the presence of glycerol in carrageenan formulation decreased the surface hydrophobicity. The contact angle of LGCR also decreased by the addition of PEG. Yuan et al. [186] also reported that PEG increased the hydrophilicity of the film. However, no significant difference in contact angle was observed between LGCR-PEG 200 and LGCR-PEG 2000. Faradilla et al. [183] studied the effect of PEG at different molecular weight (400, 1000, 2000, 4000, 8000 g/mol) as plasticizers on the contact angle of nanocellulose film. They found no difference linked to the variation in PEG molecular weights. Our results are also in accordance with those of Yuan et al. [186] who reported that PEG-plasticized films exhibited lower contact angles compared to cellulose acetate film without a plasticizer because PEG increases the hydrophilicity of the film. They argued that no significant effect of PEG molecular weight on contact angle measurements was observed.

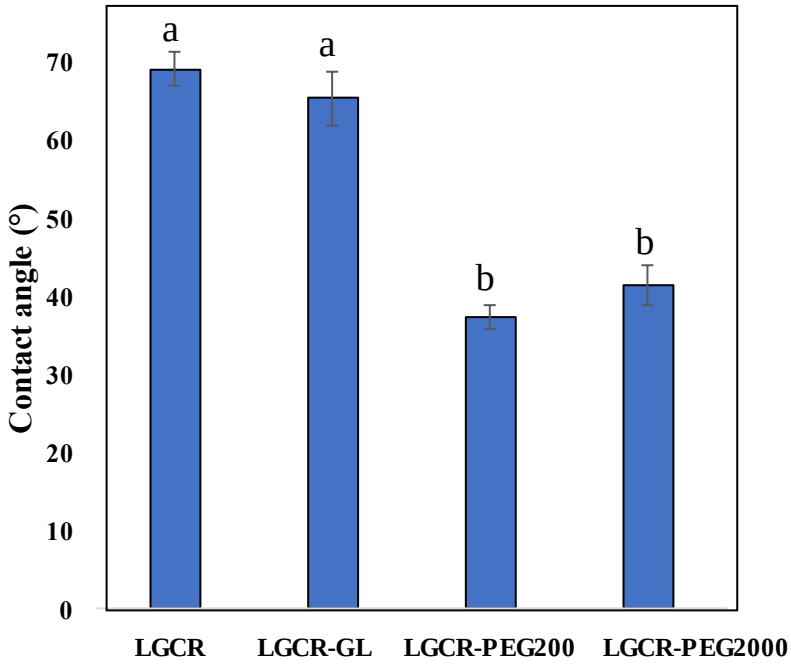


Figure III-11 : Contact angle measurements of different composite films based on lignin and carrageenan (LGCR)/glycerol (LGCR-GL), PEG 200 (LGCR-PEG 200), PEG 2000 (LGCR-PEG 2000), n=3

2.2.4. Mechanical properties

Figure III-12 and **Table III-6** show the tensile strength (TS), elongation at break (EB) and tensile modulus (EM) of the composite films. The results show that the mechanical properties of the LGCR composite film depend on the plasticizer type. **Table III-6** depicts a significant difference in the tensile modulus (EM) and tensile strength (TS) (p<0.05), while no significant difference was observed in the elongation at break (EB) (p>0.05) between different composite films. The addition of glycerol and PEG 200 to the LGCR formulation decreased the EM from 1191 kPa to 143 kPa and 887 kPa, respectively, while an increase was observed with PEG 2000 (1276 kPa). The TS of the composite films varied between 1878 and 4296 kPa. Among all samples, LGCR-PEG 2000 exhibited the highest tensile strength while LGCR-GL displayed the lowest value (LGCR-GL < LGCR <LGCR-PEG 200 < LGCR-PEG 2000). The high tensile strength of LGCR without plasticizers could be related to the presence of fatty acids in lignin from OP (discussed in the section 1.2) that can act as natural plasticizers. The blending of lignin with carrageenan in the presence of plasticizers increased the elongation at break (EB) of the films. The EB ranged between 9.37% and 16.85%, in the order LGCR < LGCR-PEG 2000 < LGCR-PEG 200 (**Table III-6**).

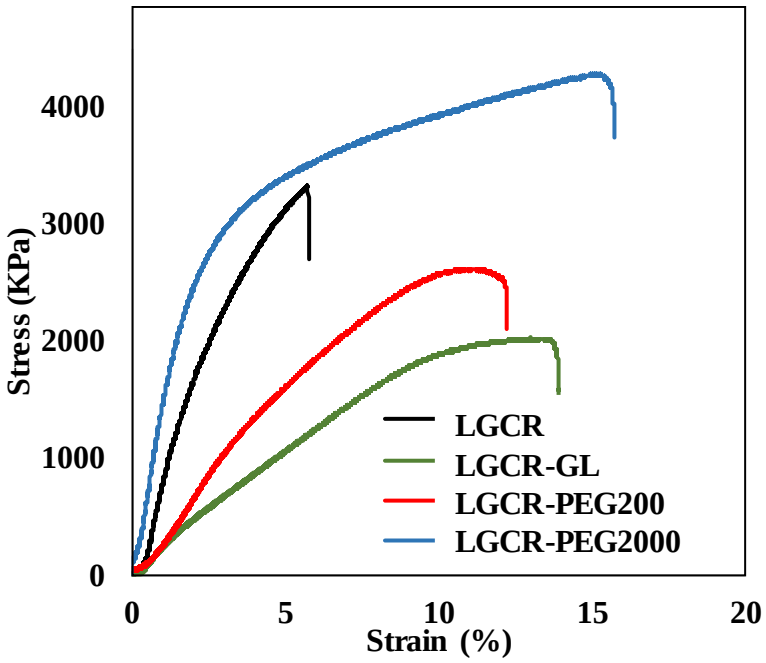


Figure III-12: Mechanical properties of different composite films based on lignin and carrageenan (LGCR)/glycerol (LGCR-GL), PEG 200 (LGCR-PEG 200), PEG 2000 (LGCR-PEG 2000), n=3

Table III-6: Tensile modulus (EM), tensile strength (TS) and elongation at break (EB) of lignin and carrageenan (LGCR)/glycerol (LGCR-GL), PEG 200 (LGCR-PEG 200), PEG200 (LGCR-PEG 2000) (n=3)

	EM (kPa)	TS (kPa)	EB (%)
LGCR	1191±356^{a}	3674±318^{ab}	9.37±1.99^{a}
LGCR-GL	143±60^{b}	1878±209^{c}	16.85±3.68^{a}
LGCR-PEG 200	887±33^{ab}	3238±192^{a}	16.85±3.60^{a}
LGCR-PEG 2000	1276±304^{a}	4296±161^{b}	16.65±4.40^{a}

The tensile strength of the LGCR-PEG 2000 film was higher than that of LGCR-PEG 200, probably due to the higher molecular weight of PEG 2000 (MW 2000 g/mol) [194], which increases the intermolecular space by reducing the hydrogen bonding interaction between lignin and carrageenan. This result is in agreement with the study reported by Cao et al. [195] who noticed an increase in the TS induced by the molecular weight increase of PEG. However, Yuan et al. [186] showed that the PEG molecular weight had no significant effect on tensile strength. Aadil et al. [194] used lignin (LG) extracted from acacia wood and alginate (AL), and PEG 4000 and glycerol (GL) as plasticizers for the preparation of LGAL, LGAL-PEG 4000 and LGAL-GL composites (LG/AL ratio: 1/4). The authors reported that TS values of LGAL-PEG 4000 (625 kPa) and of LGAL-GL (569 kPa) are higher than that of LGAL (413 kPa.) In the presence of PEG, lignin interacted with alginate by the formation of hydrogen bonds that replaced polymer–polymer interactions and impeded the formation of polymer–water hydrogen

bonds in the amorphous region [194]. In comparison, LGCR, LGCR-PEG 200, LGCR-PEG 2000 and LGCR-GL composites (our study) had higher TS values than LGAL, LGAL-PEG 4000 and LGAL-GL reported by Aadil. et al. [194]. This result is probably due to the higher lignin content in the LGCR composite formulation (LG/CR ratio of 4/1) than in the LGAL composite (LG/AL ratio of 1/4).

Figure III-12 indicates the presence of an elastic zone in LGCR/plasticizer composites, which was significantly different among the various formulations. In comparison with the other composites, the LGCR-PEG 2000 composite was characterized by an additional plastic zone and a higher elongation at break. The elasticity and plasticity give the film the capacity to extend before breaking [196]. This property could be important for a coating formulation to resist pressure without breaking during swelling [32]. The blending of lignin with carrageenan in the presence of plasticizers enhanced the elongation at break of composite films, and sometimes their Young's modulus and tensile strength. In this regard, Faradilla et al. [180] reported that glycerol increased the elasticity of nanocellulose films, but reduced the tensile strength. Our results showed that glycerol decreased both the tensile strength and elasticity of the LGCR film. For PEG 200, our findings are in accordance with those of Qussi et al. [184] who reported that the addition of PEG decreased the elastic modulus of free shellac films. Indeed, the best mechanical properties were obtained by LGCR and LGCR-PEG 2000: high Young's modulus (EM), high tensile strength (TS) and high elongation at break (EB) along with good plastic deformation. These properties could be interesting for mineral fertilizer coating formulations.

2.2.5. Thermogravimetric analysis

Figure III-13 shows that thermal degradation of the LGCR-PEG 200 and LGCR-PEG 2000 composite films was similar, but was different from those of the LGCR and LGCR-GL composite films. Generally, all composite films showed two major mass losses steps ascribed to water desorption (9-18%) in the first range of 25-200°C and a major decomposition step in the range of 200-500°C depending on the type of plasticizer. The weight loss in the first step is mainly associated with the bound and free water evaporation from the external surface and the dehydration of the intern layer, but above 150°C, the breaking of some bonds in OH groups gradually occurs. Comparing all samples in the first range of 25-110°C, the loss of water was higher in LGCR (12.19%), followed by LGCR-GL (9.87%) and LGCR-PEG 2000 composite (7.66%), whereas LGCR-PEG 200 sample had the lowest water content of only 6.86%. A higher evaporation temperature of water in films shows a stronger interaction between the film and water [197]. The stronger water retention in the LGCR-GL compared to the LGCR-PEG films was probably due to the hydrophilicity of glycerol compared to PEG [180]. However, the

samples with the lowest weight loss in the range of 200-400°C were LGCR-PEG 2000 and LGCR-PEG 200, followed by LGCR, and the largest weight loss was found in LGCR-GL-based composites. Faradilla et al. [180] also showed that glycerol reduced film thermal stability.

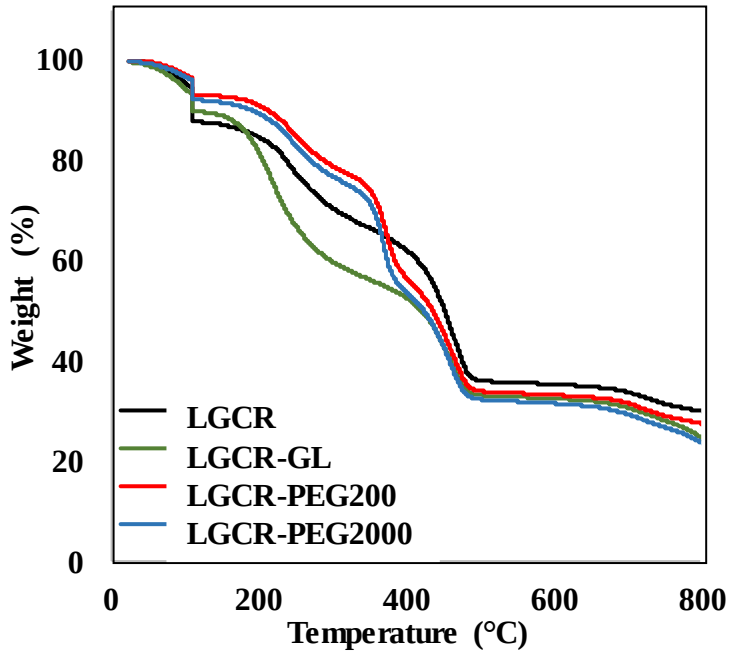


Figure III-13: TGA of different composite films based on lignin and carrageenan (LGCR)/glycerol (LGCR-GL), PEG 200 (LGCR-PEG 200), PEG 2000 (LGCR-PEG 2000), n=3

2.3.Characterization of coated TSP fertilizer

2.3.1. Morphological characterization

Figure III-14 presents a visual image of the coated TSP fertilizer granules (TSP/biopolymer ratio of 15/1 compared to uncoated TSP, which clearly indicates that TSP granules were completely covered by the film coating. The granules coated by lignin-based formulations were brown.

Figure III-15 shows the cross-sections (A and B) and whole granules (C and D) of uncoated and coated TSP fertilizer by SEM. Micrographs show good adhesion between the fertilizer and the coating. The thickness of the coating was 218±62 µm.

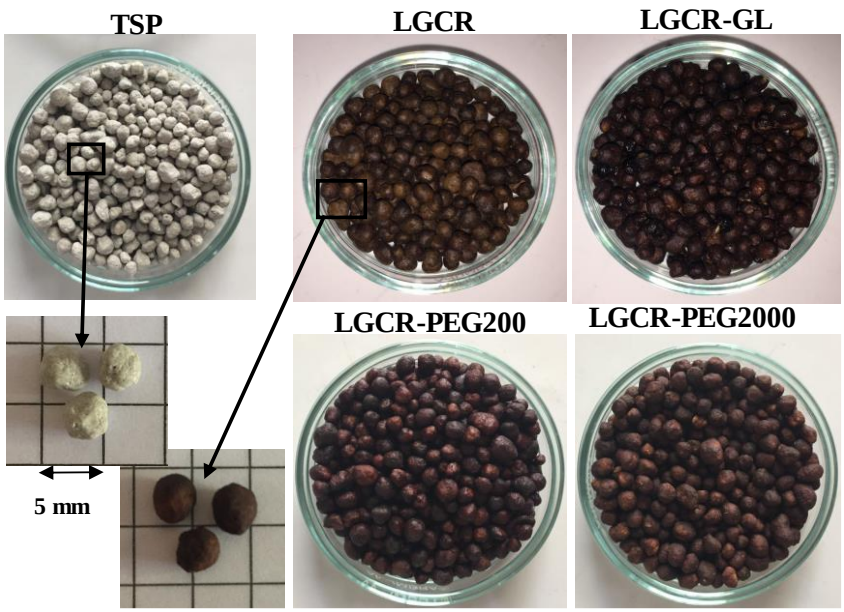


Figure III-14: Real images of uncoated and coated TSP with lignin and carrageenan (LGCR)/glycerol (LGCR-GL), PEG 200 (LGCR-PEG 200) and PEG 200 (LGCR-PEG 2000).

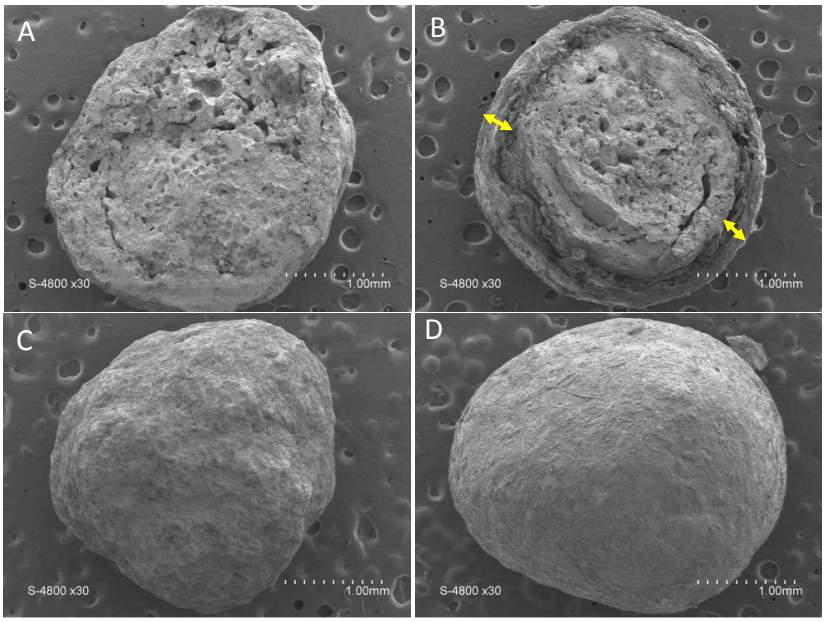


Figure III-15: SEM of cross-section of (A) uncoated TSP fertilizer (B) LGCR-coated TSP and the whole granule: (C) uncoated TSP and (D) LGCR-coated TSP.

2.3.2. Hygroscopicity

The water absorption of all formulations was also measured. **Figure III-16** shows that the water absorption increased by increasing humidity from 20% to 60% RH and with time from 0 to 3 days**.** The uncoated TSP fertilizer exhibited lower values of water absorption, while the coated TSP with LGCR and LGCR-plasticizers presented the highest values. The hygroscopicity of the TSP granules was ranked in the following order: TSP < LGCR-PEG 200 < LGCR-PEG 2000 < LGCR-GL. Faradilla et al. argued that glycerol increased moisture

sorption [183]. PEG is less hydrophilic than glycerol, which is probably why the water absorption of LGCR-PEG is lower than that of LGCR-GL [183]. In addition, plasticizers with a low molecular weight (Mw (glycerol)= 92.09 g/mol) occupy the intermolecular spaces between polymer chains and increase the free volume [185] which probably boosts the composite swelling. The same phenomenon was related by Faradia et al. [180] with glycerol-plasticized banana pseudo-stem nanocellulose film. In our work, the water absorption at 60% RH (3 days) of LGCR-plasticizers@TSP was found to be higher than that of LGCR@TSP. An increase in water absorption of 204, 293, 167 and 172% was observed for TSP coated with LGCR, LGCR-GL, LGCR-PEG 200 and LGCR-PEG 2000 compared to the uncoated TSP granule. This high water absorption of the LGCR-plasticizers@TSP might be due to the low degree of cross-linking between the lignin and carrageenan molecules in the presence of plasticizers.

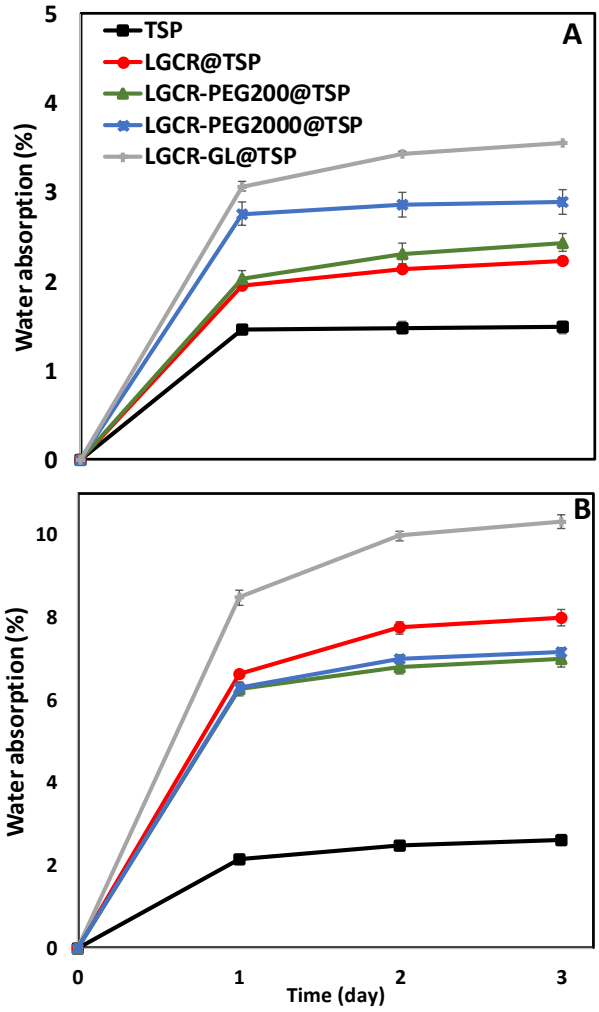


Figure III-16: Water absorption (WA) of uncoated and coated fertilizers over time at different relative humidity levels: (A) 20% and (B) 60% with lignin and carrageenan (LGCR)/glycerol (LGCR-GL), PEG 200 (LGCR-PEG 200), PEG 200 (LGCR-PEG 2000), n=3.

2.4.Release behavior of phosphorus from coated TSP fertilizers

To evaluate the performance of the composite films from different formulations developed in this study, the release of P from uncoated TSP and coated TSPs with different formulations was studied in water over 30 days. Among the fertilizers, TSP showed the highest phosphorus (P) release, with 85% ± 14 and 95% ± 4 P released within 1 and 2 days, respectively, and P was completely dissolved after 3 days (**Figure III-17**). LGCR with or without plasticizers exhibited the slowest P release. The amounts of phosphorus released at 1 day from LGCR/plasticizers@TSP ranged from 39 to 81 %. TSP@LGCR exhibited the lowest value while LGCR-PEG 2000@TSP exhibited the highest one. The P release from different coated TSP granules with different formulations was ranked in this following order LGCR < LGCR-PEG 200 < LGCR-GL < LGCR-PEG 2000. After 2 days, LGCR@TSP released 56%, while LGCR-PEG 200@TSP, LGCR-GL@TSP and LGCR-PEG 2000@TSP stabilized at 71% and 79%, respectively. The LGCR-plasticizer formulations did not decrease the release of P compared to the LGCR formulation. This is most likely due to the hydrophilic behavior of the plasticizers [183]. The transition from the linear release stage to a constant phase started at day 2 for LGCR@TSP and at day 1 for the others. From the second day, the release behavior curve of P from all coated TSPs stabilized and the amount of P released remained the same throughout 30 days. This suggests that P release is hindered by some phenomena other than diffusion resistance. This could be related to the P saturation in water that is quickly reached due to the high porosity of the films or by the interactions between salts in the original fertilizer [198].

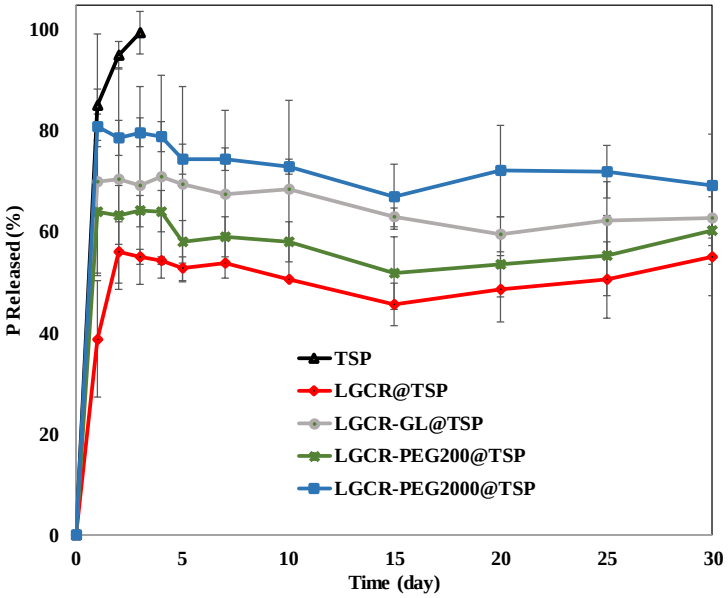


Figure III-17: Release of phosphorus in water from TSP and coated TSP fertilizers with lignin and carrageenan (LGCR)/glycerol (LGCR-GL), PEG 200 (LGCR-PEG 200), PEG 200 (LGCR-PEG 2000), n=3.

2.5. Correlations between the P release behavior and the physicochemical properties of coating films

The correlation matrix (**Table III-7**) was constructed to correlate the P release behavior to the coating films properties. The results show that P release is negatively correlated with elastic modulus (r= -0.2, *p*=0.62), while it is strongly positively correlated with elongation at break (r=0.91, *p*=0.001). A moderately negative correlation between P release and CA was also revealed (r= -0.61, *p*=0.1), while the opposite was observed between P release and WA (r=0.73, *p*=0.03). The same correlation trends between P-release and the coating properties were also reported and well discussed in the first part. The high elasticity of the coating materials allows the shell to resist the internal pressure created inside the core upon contact with water, and P is released slowly without the destruction of the shell. In addition, the high hydrophobicity of the coating materials prevents the penetration of large quantities of water inside the fertilizer core and then decreases the dissolution of TSP.

Table III-7: Correlation matrix between the properties of composite films and coated TSP. Film properties: EM (elastic modulus), TS (tensile strength), EB (elongation at break) and CA (contact angle). Coated TSP properties: P release within 1 day and WA (water absorption at RH 20% within 1 day).

	P-release	EM	TS	EB	CA	WA
P-release	1					
EM	-0.2	1				
TS	-0.02	**0.98*** **	1			
EB	**0.91** **	-0.43	-0.28	1		
CA	-0.61	-0.35	-0.44	-0.64	1	
WA	**0.73***	-0.58	-0.43	0.61	0.09	1

p-value for correlations significance: (***) < 0.001; (**) < 0.01; (*) < 0.05.

Table III-8 compares the results of this part 2 to other previous studies using biopolymers and plasticizers as coating materials. According to Lubkowski et al. [62], the addition of glycerine to chitosan biopolymers decreased the NPK release. As the plasticizer content is high, the NPK release is low. Liu et al. [22] reported that the coating of the urea using starch acetate and triacetin plasticizer decreased N release to 56.5% within 1 day compared to 79.9% in the case of uncoated urea. Perez Garica et al. [21] argued that ethyl cellulose-dibutyl sebacate, and ethyl cellulose-dibutyl phthalate coated N had similar N release profiles. Mulder et al. [161] also used lignin with plasticizers and some other hydrophobic compounds and reported that complete nitrogen release through these coating materials still occurred within less than 1 h. In our work, we showed that the addition of plasticizers didn't decrease the P release rate, and that the use of lignin-carrageenan biopolymers alone as coating showed a decrease on P release to 38%

within 1 day, compared to 85% for uncoated P fertilizer. It can be concluded that our study is interesting in that we used low-cost materials based on OP, which can potentially be a good candidate for coating fertilizers and slowing the decrease on P release rate without adding commercial plasticizers.

Table III-8: Comparative studies of different works using polymers and plasticizers as coating materials to control nutrient release

Coating materials	Plasticizers added	Fertilizer	Coating method	thickness (μm)	P release rate (%)	Reference
Lignin-carrageenan (LGCR)	Glycerol PEG 200 PEG 2000	P	Coating pan	218	**Uncoated:** 85% within 1 day **Coated with LGCR** : 38% within 1 day **Coated with LGCR+plasticizers**: 63- 81 % within 1 day	This work
Chitosan	glycerine	NPK	-	47-542	**Uncoated:** 100% within 1 hour **Coated with chitosan** : 95% within 5 hours **Coated with chitosan**+glycerine: 64%-96.5% within 5 hours	Lubkowski et al. [62]
Starch acetate (SA), carboxymethyl starch/xanthan gum (CMS/XG)	triacetin	N	Coating pan	_	**Uncoated**: 79,9% in 1 day **Coated with SA+triacetin**: 56.5 and 100% in 1 and 5 days **With SA+ CMS/XG**: 100% in 10 day	Lu et al. [22]
Ethylcellulose (EC)	dibutyl sebacate (DS) Dibutyl phthalate (DP)	N	fluidized-bed	-	**Uncoated**: 100% within 1 hour **Coated with EC**: 100% within 40 hours **Coated with EC+DS/DP:** 66% within 40 % hours	Peréz-Garcia et al. [21]
Lignins	Glycerol, Lupranol, Acronal, Styronal, sorbitol, PEG400, PEG2000, PEG6000	N	Coating pan	-	**Noncoated** >80% after 30 min **Coated** 60-80%after 30 min	Mulder et al. [161]

3. Conclusion

This chapter reports the potential of lignin extracted from OP biomass with polysaccharides/plasticizers as a new coating material for water-soluble TSP fertilizer. In the first part, films containing lignin and carrageenan showed the best mechanical properties. The blending of lignin with polysaccharides reduced the hydrophobicity of the composites compared to that of the pure polysaccharide films but still showed higher hydrophobicity than

the lignin film. The coating materials based on lignin and polysaccharides appear to have a good interaction with the mineral fertilizer surface, confirming the effect of different formulations on the delay of P release. The results showed that more than 95% of P was released from uncoated TSP within 48 h, and 100% of P was released within 72 h, while the release of P with the lignin-polysaccahrides@TSP formulations decreased to approximately 60% within 72 h with a TSP/polymer ratio of 5/1. In the second part, the effect of different plasticizer types on structural, thermal, mechanical and surface properties of plasticized lignin-carrageenan film composites was also evaluated and compared. The results showed that the hydrophobicity of the composites decreased with increasing plasticizer addition. The addition of plasticizers also decreased the elasticity of all films except PEG 2000. These formulation composites used as coating materials for TSP fertilizers to decrease the release of phosphorus were also investigated in water. The coating materials decreased the P release from 100% within 3 days for uncoated TSP to 55% - 69% within 30 days in the case of the coated-TSP granules. However, the type and molecular weight of plasticizers had no significant effect on phosphorus release in water. The correlation matrices reveal the dependence of phosphorus release on the elasticity of the material, its elongation, hydrophobicity and absorption of water.

In the next chapter, the dissolution of formulated fertilizers (developed in this chapter) in a carbonated soil matrix will be performed and the study of their effects on chemical and biological soil properties will be made. The main chosen formulations were uncoated TSP, lignin@TSP and and lignin-carrageenan@TSP. The choice of coated TSPs is justified by the fact that lignin is the base material that has been used in all the formulations. For lignin-carrageenan@TSP, it was chosen because of its low P release behavior in water.

CHAPTER IV. Coated TSP based on biopolymers: effect on chemical and biological soil properties

1. Introduction

In this chapter IV, the dissolution of coated fertilizers in a carbonated soil matrix was performed and the study of their effects on chemical and biological soil properties was made. The main objective is to investigate if the coating affects the dissolution of TSP in the soil and if the coated fertilizers influence the soil properties compared to the uncoated fertilizer. Two scientific approaches have been adopted; the first consists in studying the spatio-temporal effect of these fertilizers on soil pH using optodes techniques and the second in quantifying different forms of phosphorus (available phosphorus, microbial phosphorus) and total phosphorus as well as phosphorus recovery at different distances from fertilizers application.

2. The dynamics of soil pH with uncoated and coated TSP fertilizer

The control soil had a pH of 7.8±0.2 throughout the 28 days of incubation and in all position of the petri-dish (**Figure IV-1**). Statistical analysis (mixed models and multiple comparison tests) showed no significant effect of time and distances 0 to 35 mm (S0 to S4) on soil pH ($p > 0.05$) (data not shown). The distances > 35 mm (S5 and S6 edges) were not integrated due to problems with the optode-soil contact.

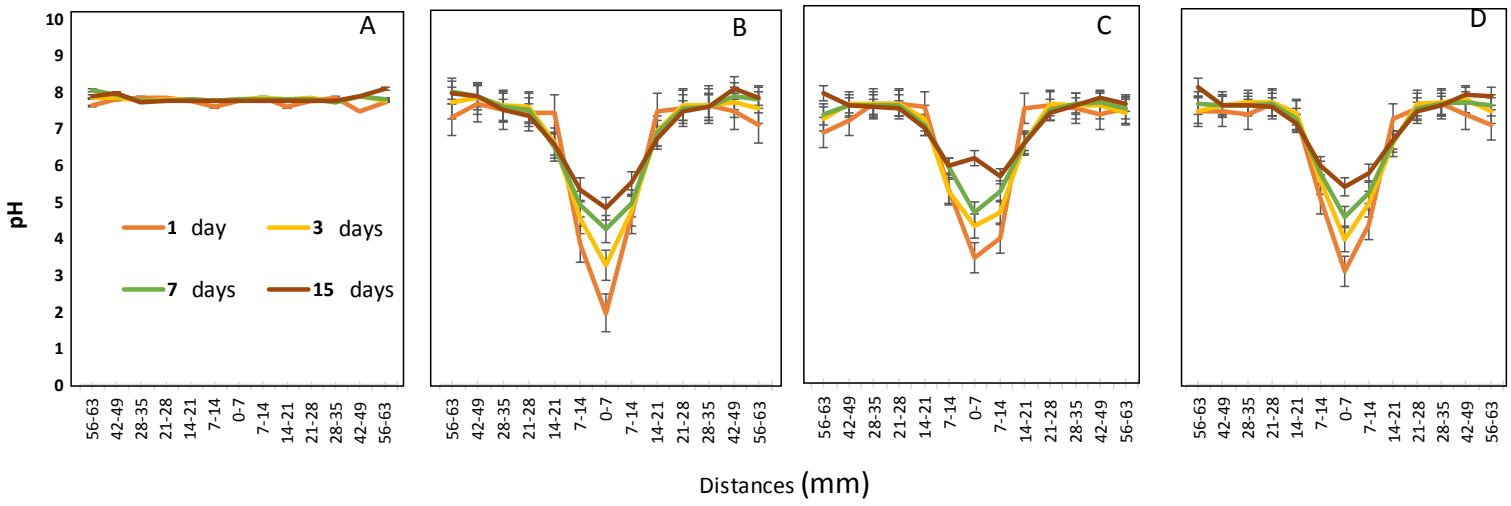


Figure IV-1: Spots measurements of soil pH as a function of time (measurements at days 1, 3, 7 and 15) and the distance from the added granule for: A) no-TSP fertilizer (control), B) uncoated TSP, C) lignin@TSP and D) lignin-carrageenan@TSP , n=4

With the addition of TSP fertilizers, a strong acidification in the soil located directly around the granule was observed with a pH drop of more than 4 pH units compared to unfertilized soil (**Figure IV-1**). The decrease in soil pH was probably caused by the low pH of TSP (pH of the saturated solution of TSP<2). Statistical analysis of pH values of soil treated with uncoated and coated fertilizers (without control) showed a significant effect of fertilizer treatment, distance

from the granule and time on the measured soil pH (**Table IV-1)** and a significant effect of their interaction (in pairs or all three).

Table IV-1: Results of mixed model analysis on pH, in function of the treatment (uncoated and two coated TSP), the section (distances to fertilizer) and time

	Treatment	Distance	Time	Treatment × distance	Treatment × time	Distance × time	Treatment × distance × time
pH (n=5850)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

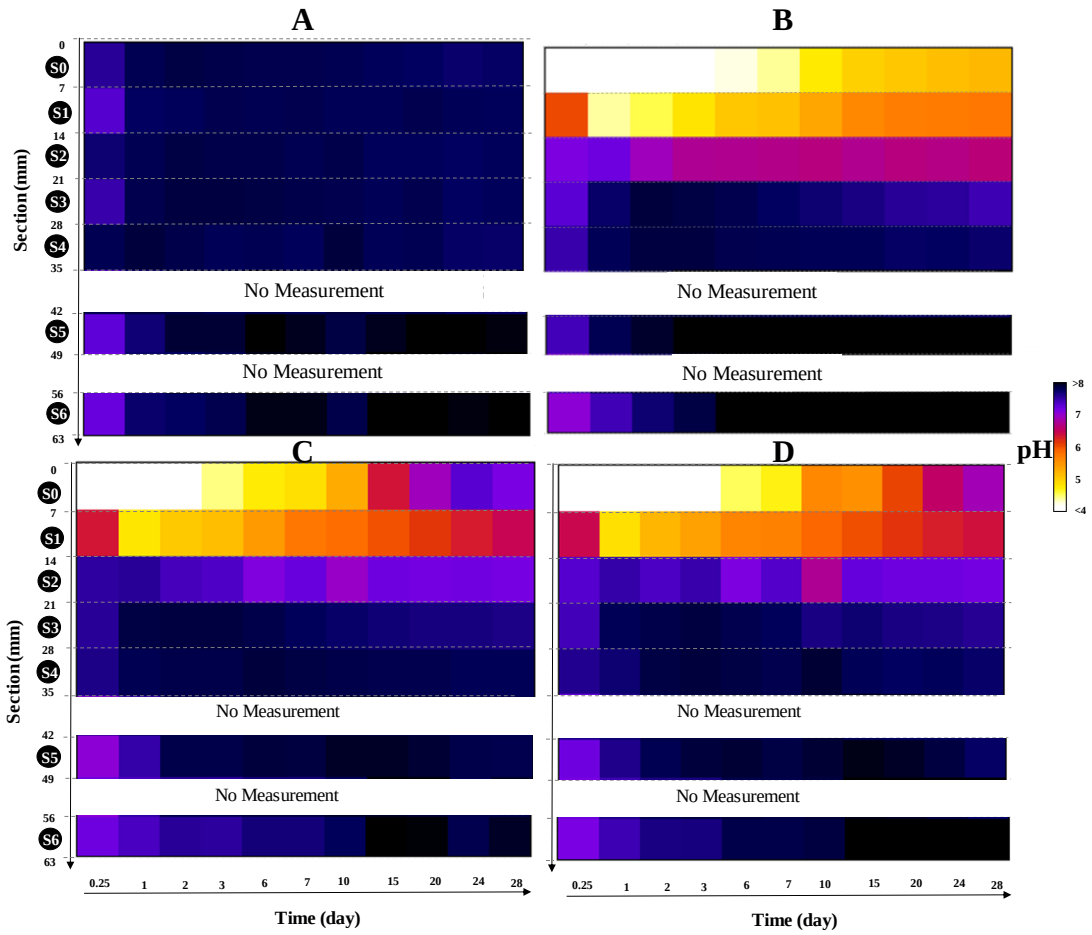


Figure IV-2: Soil pH data converted to images with scale, using imageJ software: A) soil with no-TSP fertilizer (control), B) soil treated by uncoated TSP, C) soil treated by LG@TSP and D) soil treated by LGCR@TSP, n=4

The soil acidification caused by the coated TSPs was significantly lower compared to the uncoated TSPs, while no significant difference was observed between the two coated treatments lignin@TSP and lignin-carrageenan@TSP. The effect of fertilizers treatment on soil pH over

time was significant at distance < 21 mm from the fertilizer application. For uncoated TSP, pH decreased dramatically after 1 day from 7.8 (pH of the soil control) to 2.6 above the granule (distance 0-7 mm), while coated TSP decreased to 3.8, which was an increase of 1.2 pH unit compared to uncoated TSP and a decrease of 4 pH unit compared to the soil control. The acidification caused by fertilizer treatments has reached the distances 7-21 mm. Over 21 mm, the pH was almost similar to the soil control for all fertilizers treatments (data not shown). The area affected by the fertilization remains acidic with a slight increase in pH over time, highlighted in the **Figure IV-2.** The average pH of each of the two symmetrical sections has been reported. S0 is the most acidified region, followed by S1 and S2. When the pH of S0 and S1 rises, pH of S2 falls moderately. The decrease in pH of the soil treated with coated fertilizers is limited in the 0-14mm region and the pH starts to rise again from the 3rd day while the acidification caused by uncoated TSP still high during all the incubation time, with a little increase in pH from day 7. The faster pH recovery for soils treated with coated fertilizers compared to TSP could be related to the basic nature of the coating. In fact, the lignin used in coating formulations was extracted from olive pomace residue [199] using sodium hydroxide that is strongly alkaline [200,201].

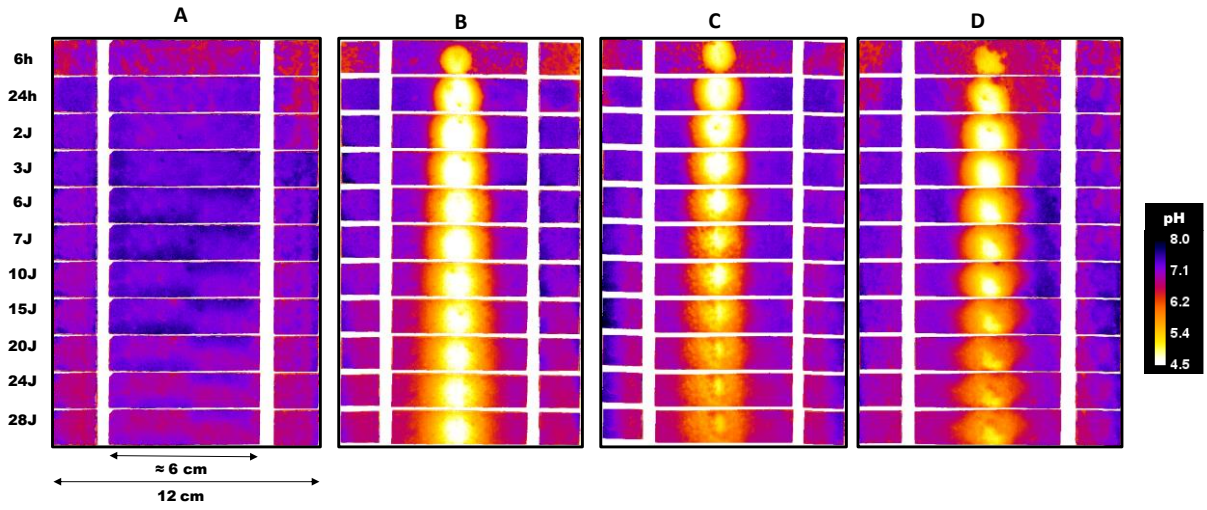


Figure IV-3: Planar pH optode measurements during 28 days of soil pH dynamics treated by: A) no-TSP fertilizer (control), B) uncoated TSP, C) LG@TSP and D) LGCR@TSP, n=1

Planar optodes 2-D representation (**Figure IV-3)** highlights the same phenomenon observed by the spots but offers a spatial representation of pH changes, which confirms the results discussed previously.

The control had a homogeneous spatio-temporal distribution with a pH around 7.7, which is in good agreement with spots results. The soil treated with the TSP granule showed a circular and isotropic soil acidification (with a radius of 7 mm) around the granule after 6h. Over time, the

patch was expanding. The acidification caused by the TSP granule reached 14 and 21 mm from the granule center after 3 and 28 days, respectively. With coated TSPs, the soil acidification continued to expand slightly around the granule up to a radius of 14 mm, while the soil pH above the granule gradually increased after 3 days, to reach a value in the range of 6-6.5 after 28 days compared to 4-4.5 for TSP. The planar optodes confirmed the diffusion symmetry in a circular radius around the fertilizer. Lombi et al. [24] reported that in a calcareous and a non-calcareous alkaline soil, the pH of the soil treated with TSP and monoammonium phosphate (MAP) granules dropped by 0.8-0.9 pH units at a distance of 13.5 mm from the fertilizer and by <0.2 pH units at a distance of 25.5 mm, while no significant change was observed beyond 25.5 mm. The authors argued that the decrease in soil pH is probably caused by the low pH of TSP and monoammonium phosphate MAP (the pH of their saturated solution is <2 and 3.5, respectively), and the nitrification of the NH_4 present in the MAP fertilizer [202,203].

The initial soil pH partly governs the soil pH change in response to fertilizer additions [203] due to proton exchange . According to Lombi et al. [24], the soil pH after fertilizers application dropped by less than 1 pH unit and the acidification was limited due to the high buffering capacity of carbonates in the calcareous soil. In our study, the soil pH dropped by more than 4 pH units for samples treated with TSP. This difference could be related to both the amount of P applied and the lower $CaCO_3$ content in our soil. Moreover, the pH measurements method may contribute to these differences as with optodes, the pH was measured at the surface of the upper layer of soil (which was close to the fertilizer application), whereas Lombi et al. measured the pH in solution thus including the whole soil layers less affected by the fertilizer. However, although absolute values differ, both studies presented similar patterns of soil pH variation under the influence of TSP granules.

3. Dynamic of phosphorus pools

The resin-P after 28 days from the fertilizers application was significantly greater ($p < 0.05$) in the 21 mm near fertilizer application (S0, S1 and S2) compared to the untreated soil, while no significant effect was observed after 21 mm (S5 and S6) **(Figure IV-4)**. This results is in agreement with Culleton et al. [204]. Among fertilizer treatments, no significant difference was observed, except at 14 mm (S2) with lower resin-P in the soil with uncoated TSP than for lignin@TSP. Concerning coated TSPs, no significant difference on resin-P was observed between lignin@TSP and lignin-carrageenan@TSP at different distance from the granule application. The resin-P generally decreased with the distance from the granule. There is a tendency that uncoated TSP had a rapid release of P compared to coated fertilizers which was

well visible in water solution [199] and less detectable (non-significant) in the soil. Beyond 21 mm from the granule, no effect was observed.

The short range of the effect of the fertilizers is likely linked to precipitation reactions of P from the TSP with soil ions. In calcareous soils, the dominant reaction is precipitation with Ca and Mg [203,205]. While in non-calcareous soils, P adsorption on the surface of Fe and Al hydroxides is prevailing [206]. In our case, biopolymers-based coatings did not improve the resin-P availability from TSP. Some works used sulfur as a coating agent because it reduced pH around the granule due to the oxidation phenomenon, which could improve the solubilization of Ca precipitated phosphates in soils [207]. Nascimento et al. [203] studied the effect of uncoated and sulfur/humic acid-coated MAP on labile P during 56 days. The authors reported that in a calcareous soil, there was no significant difference on soil available P between uncoated MAP and humic acid@MAP treatments, while a significant difference was observed with sulfur@MAP, which exhibited the highest value of the available P. In contrast, in an acidic soil, humic acid@MAP and sulfur@MAP increased the available P concentration more than uncoated MAP.

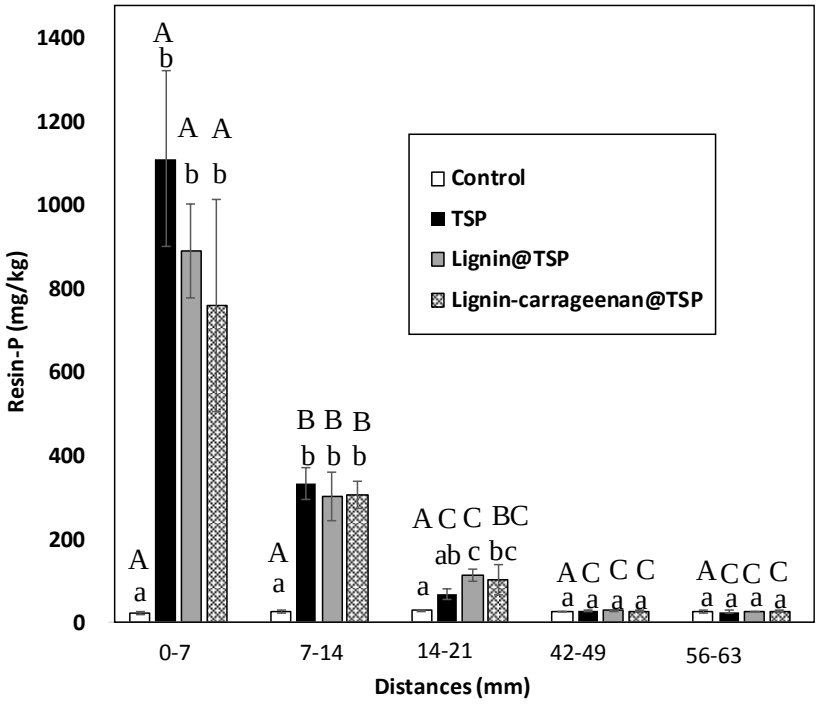


Figure IV-4: Resin-P as a function of treatment and distance from granule (section), after 28 days of incubation. Small letters indicate significant differences ($p < 0.05$) among treatments within the same distance. Capital letters indicate significant differences ($p < 0.05$) among distances for the same treatment. Error bars represent standard error.

Microbial P was measured after 28 days of fertilizer application between 14 and 56 mm from the granule center (S2, S5 and S6) **(Figure IV-5)**. Microbial-P was insignificantly different

among the fertilizer treatments. Within 49 mm (S5 and S6), the effect of fertilizer treatments was not significantly different to that of the control. The application of P fertilizers tends to increase the microbial-P at a distance of 21 mm (S2), however, the effect was insignificant compared to the control except for LGCR@TSP. The increase in the microbial biomass P is expected to enhance the P availability in soil as this pool acts both as a sink and source of plant nutrients [208]. Sugito et al. [209] showed also an increase on the microbial biomass P after the application of NPK chemical fertilizer, cow manure compost or sewage sludge compost with no significant difference among these amendments. Clarholm [210] and He et al. [211] reported that the application of P fertilizers impacted the P content of soil microbial biomass. Because coated TSPs exhibited the highest microbial P, it supports the hypothesis that the decomposition of polymeric coatings (rich in carbon) by microorganisms would result in phosphorus immobilization by soil microorganism.

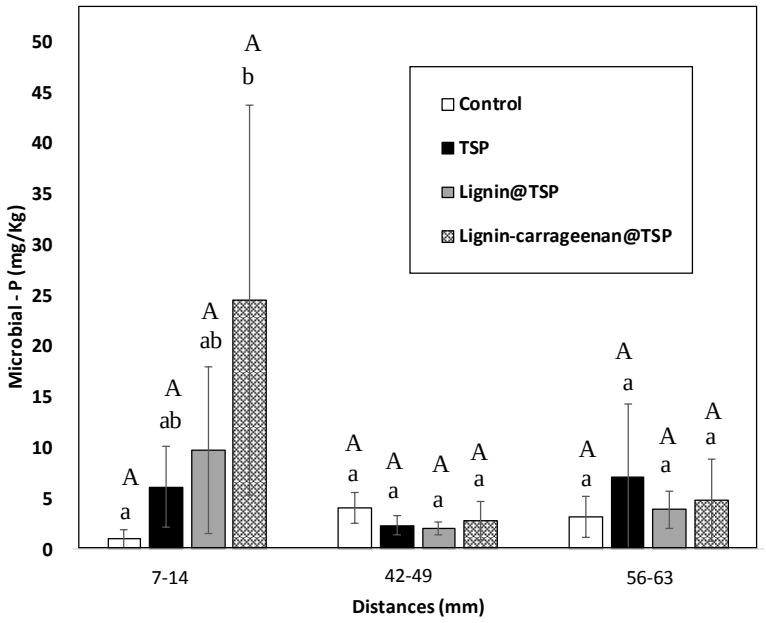


Figure IV-5: Microbial-P as function of treatment and section, after 28 days of incubation. Small letters indicate significant differences ($p < 0.05$) among treatments within the same section. Capital letters indicate significant differences ($p < 0.05$) among distance for the same treatment. Error bars represent standard error.

The remaining P varied insignificantly ($p > 0.05$) between treatments and significantly ($p < 0.05$) with the distance i.e. across sections (**Figure IV-6**). Most fertilizer's P (>64%) remained within the first 7 mm of P granule center (S0) and less than 19% was spread to 7-21 mm (S1 and S2) while nearly no added fertilizer P was found beyond 21 mm from the fertilizer application point. There is no significant effect on P recovery between uncoated and coated TSP. Castro et al. [121] showed close results with MAP and polymer-coated MAP. The authors

argued that approximately 80% of the P recovery is associated to the first 0-7.5 mm section near fertilizer application while 10% and 6% was found in the second (7.5-13.5 mm) and third (13.5 – 25.5 mm) sections. In agreement with the present study, they found that the polymeric coating did not impact the P migration, Similarly Fink et al. [212] and Lombi et al. [24] reported that the P recovery of applied P fertilizers in the center of a petri dish, is concentrated in the inner zone of a 13 mm.

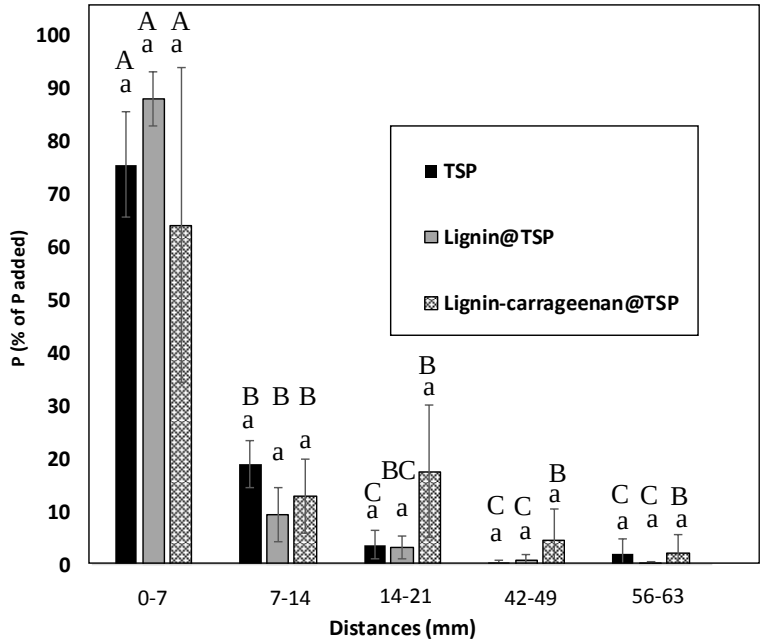


Figure IV-6: P recovery (%) in function of treatment and section, after 28 days of incubation. Small letters indicate significant differences ($p < 0.05$) between treatments among the same section. Capital letters indicate significant differences ($p < 0.05$) between distances using the same treatment. The bars represent standard error.

4. Conclusion

Biopolymers-coated phosphorus (P) fertilizers have shown promoting results in reducing the P release. However, their dissolution behavior has mainly been studied in water and less in the soil matrix. In addition, their impact on the soil quality are rarely addressed. The aim of our work was to compare the P diffusion from uncoated TSP and biopolymers-coated TSP fertilizers in a Mediterranean soil, and to evaluate their effect of on some chemical and biological soil properties. The first 20 cm of soil were sampled from a cropped site in South-West France and experiments were carried out on petri dishes within 28 days, with different fertilizers treatments (No fertilizer, uncoated TSP, lignin@TSP and lignin-carrageenan@TSP). Spatial and temporal pH variations of the fertilized soils were investigated and different pools of P (available P, microbial P and P recovery) at different distance from the granule application

were determined. Results showed that the coated TSPs acidified the soil at a radius of 14 mm around the fertilizer granule, while the acidification has spread to 21 mm with the uncoated TSP. Moreover, there is a tendency of increasing microbial-P in the soil treated with coated TSP due to the carbon input and a tendency of a rapid release of P from uncoated TSP compared to coated TSP due to the coating barrier. The P recovery results showed a P migration in the 21 mm from the granule application with no significant effect between fertilizers treatments.

GENERAL CONCLUSION

General conclusion

The central objective of my thesis was to study whether phosphate fertilizers coated with lignin extracted from olive pomace biomass, and other biopolymers from seaweeds or lignocellulosic materials as well as plasticizers is endowed with dissolution and degradation characteristics in soil that could improve their efficiency. Another main objective is to understand the relationship between the coating agents' properties and the phosphorus release through these coatings. The central hypotheses of this work were: i) the physicochemical properties of coating formulations may govern the phosphorus release behavior from coated phosphorus fertilizer, ii) the application of fertilizers coated with carbon-rich biopolymers would affect the chemical and biological properties of the soil (i.e. soil pH and different forms of phosphorus). These questions led to research strategies and studies organized in three major steps: i) formation and characterization of composite films based on biopolymer formulations, ii) coating and characterization of TSP phosphate fertilizers, iii) study of their dissolution in the soil, and their effect on chemical and biological soil properties.

The first step was performed using lignin, k-carrageenan, sodium carboxymethylcellulose and sodium alginate biopolymers (alone or combined) and some plasticizers (glycerol, polyethylene glycol). These films have been characterized for their structure, hydrophobicity, mechanical properties, thermal and water stability. The second step was conducted using the same formulations of films and with a coating system that we have developed. These fertilizers have been characterized for their morphology, thickness of the coatings, hygroscopicity and phosphorus release in water. The third experiment was performed in a cropped soil under controlled laboratory conditions in petri dishes. The chosen formulations based on their slow release behavior in water was studied for their dissolution in the soil, and their effect on soil pH and on different pools of phosphorus (available P, microbial P and total P).

Films formulations based on lignin extracted from olive pomace and the other commercial biopolymers were successfully prepared. Lignin-carrageenan formulations showed the best mechanical properties. The blending of lignin with polysaccharides reduced the hydrophobicity of the composites compared to that of the pure polysaccharide films but still more hydrophobic than the lignin film. The results showed that more than 95% of P was released from uncoated TSP within 2 days, and 100% of P was released within 3 days, while the release of P with the lignin-polysaccahrides@TSP formulations decreased to approximately 60% within 3 days. The hydrophobicity of the composites decreased with increasing plasticizer addition. The addition of plasticizers also decreased the elasticity of lignin-carrageenan-plasticizers films except PEG 2000. The coating materials-based plasticizers decreased the P release from 100% within 3 days for uncoated TSP to 55 - 69% within 30 days in the case of the coated-TSP granules. However,

the type and molecular weight of plasticizers had no significant effect on phosphorus release in water. The correlation matrices reveal positive correlations between phosphorus release and the elongation of coatings and their water absorption, while negative correlations were found between phosphorus release and the elasticity and hydrophobicity of coatings.

Our study in the soil showed that the biopolymers-coated TSPs dissolves differently compared to uncoated TSP, with almost similar dissolution behavior of lignin@TSP and lignin-carrageenan@TSP. Both uncoated and coated TSPs acidified the soil near the fertilizer granule application. The decrease in pH of the soil treated with coated fertilizers is limited in the 0-14 mm region and the pH starts to rise again from the 3rd day while the acidification caused by uncoated TSP spread to 21 mm and still high during all the incubation time, with a little increase in pH from day 7.

The available P showed high concentration in the first 21 mm from the granule application after 28 days, with a tendency of a rapid release of P from uncoated TSP compared to coated TSP. The application of coated P fertilizers tends to increase the microbial-P at a distance of 14 mm compared to uncoated TSP. Most fertilizer's P (P recovery (%)) remained within the first 7 mm of the granule application with no significant difference among treatments.

The following is a summary of the main conclusions related to the questions/hypotheses discussed above in the "objectives and hypothesis" section:

- The coating reduces the P release in water.
- The nature of the biopolymers influenced the properties of the coating agent and the P release behavior.
- The P release rate depended on the thickness of the coating, its elasticity, elongation, hydrophobicity and water absorption.
- The addition of plasticizers to the formulations didn't decrease the P release.
- Compared to uncoated TSP, coated TSPs acidify the soil over a smaller radius.
- An increase on microbial-P was observed in the soil treated with coated TSP
- A slower release of P on soil was observed with coated TSP compared to uncoated TSP.

Many perspectives for this study can be considered. Firstly, we suggest using and comparing lignins from different lignocellulosic biomass and different methods of extraction (organosolv, soda/anthraquinone, hydrotrope, etc.). These lignins will have different properties (i.e. in term of their porosity, hydrophobicity, mechanical properties, etc.) and will probably behave differently as coatings. Secondly, we also suggest testing fluidized bed as a coating method and comparing the coating quality with the rotating pan process. The calculation of the energy

consumed by the two coating techniques and estimating the material losses will also help to decide which technique is the most efficient energetically and economically. Last but not least, another perspective is the study of life cycle assessment for evaluating environmental impacts associated with all the stages of the life cycle of our coated fertilizers.

As our experiments were carried out with a calcareous soil in petri dishes, we suggest testing another soil type with contrasting properties and comparing the behavior of coated fertilizers in the both soils. In addition, we suggest carrying out experiments in the field in the presence of plant to study the efficiency of the coated fertilizer.

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ANNEXES

ACS Sustainable Chemistry & Engineering

Research Article

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Properties of Coated Slow-Release Triple Superphosphate (TSP) Fertilizers Based on Lignin and Carrageenan Formulations

Saloua Fertahi,[†,‡,§,⊥] Isabelle Bertrand,[†] M'Barek Amjoud,[‡] Abdallah Oukarroum,[§] Mohamed Arji,[∥] and Abdellatif Barakat*[,§,⊥]

[†]Eco&Sols, Université de Montpellier, CIRAD, INRA, IRD, Montpellier SupAgro, 2, Place Pierre Viala, 34060 Montpellier, France

[‡]LMCN, Faculté des Sciences et Techniques Guéliz, Université Cadi Ayyad, 40000 Marrakech, Morocco

[§]Mohammed VI Polytechnic University (UM6P), Hay Moulay Rachid, 43150 Ben Guerir, Morocco

[∥]OCP/Situation Innovation, OCP Group, Jorf Lasfar Industrial Complex, BP 118 El Jadida, Morocco

[⊥]IATE, Université de Montpellier. CIRAD, INRA, Montpellier SupAgro, 2, Place Pierre Viala, 34060 Montpellier, France

ABSTRACT: Coated triple superphosphate (TSP) fertilizer with slow-release and water retention properties was prepared using lignin extracted from olive pomace (OP) biomass and k-carrageenan biopolymer. The aim of this work was to develop coating formulations that serve as a barrier to phosphorus diffusion through TSP fertilizers. Different formulations of lignin and k-carrageenan with or without polyethylene glycol (PEG 2000) were prepared. The chemical composition and morphological, mechanical, and surface properties of different formulations were characterized and compared. The blending of lignin with carrageenan in the presence of PEG enhanced the tensile properties of the formulation. Indeed, the mechanical properties of different formulation composites are classified in the order of lignin-carrageenan-PEG > lignin-carrageenan > lignin. After 6 h in water, the lignin@TSP formulation released two times less phosphorus (P) than the uncoated TSP. Lignin-carrageenan@TSP and lignin-carrageenan-PEG@TSP released only 28.21% and 13.51%, respectively, of phosphorus after 6 h compared to 72% for uncoated TSP. Indeed, lignin-carrageenan-PEG@TSP absorbs more water than TSP. The addition of plasticizer did not significantly modify the mechanical properties of the formulation composites. In the future, these products will be tested to evaluate their impact on chemical and biological soil properties.

KEYWORDS: *Phosphorus, Coating, Composites, Soil, Lignin, Fertilizers slow release*

INTRODUCTION

Phosphorus (P) is an essential nutrient for life, and its management is a problem that affects global food security.[1] Its bioavailability in soils affects plant growth and net primary production. Soil P is often limiting, not because the amount of total P in soil is low but rather because P in soils is in chemical forms that are not available to plants.[2,3] With the increase in the world population over the years, the demand for P fertilizers is increasing, while access to its sources is becoming uncertain due to limited resources and geopolitical concerns.[4] The world phosphate fertilizer demand is expected to reach 46600000 tons in 2018, while it was 41700000 tons in 2013 and 42700000 tons in 2014.[5] However, due to the low efficiency of soil P fertilizers, only 10−20% of P is taken up by the plant.[6−8] The currently available forms of P fertilizers require further improvements to increase their bioavailability in soils.

Recently, controlled release fertilizer (CRF) has been developed to increase the bioavailability of P fertilizers in soils.[9] The efficiency of P CRFs is usually greater than that of conventional fertilizers.[10] Coating with an insoluble material is one of the methods commonly used for CRF formulations.[11] Although the release mechanism in soil is not well understood, it depends on many factors, such as the nature of the coating materials, their porosity and thickness,[12,13] the soil type, its moisture, its pH, and microorganism activities.[14−17] Synthetic polymers are considered potential and attractive candidates for mineral fertilizer coating. Some of the synthetic polymers most commonly used in the literature are polyethylene,[18−20] poly(*N*-isopropylacrylamide),[21,22] polyurethane,[21] polysulfone,[12,13,23,24] polyacrylonitrile,[12,13] etc. However, these polymers have shown many drawbacks, such as their high prices and their negative effects on the environment. Most synthetic polymers are currently based on the use of expensive multistep chemical processes. These processes consume large amounts of organic solvents (e.g., *N*-dimethylformamide[12] and chloroform[25]) and generate significant waste (e.g., effluents) that is harmful to the environment. The use of little or no solvents and chemicals for formulating CRF technology can decrease the effluents generated and the cost and reduce soil

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pollution. According to Trenkel,[26] the use of polymeric materials in coatings could lead to an undesirable accumulation of plastic residues of up to 50 kg/ha/year. To overcome these economic and environmental issues, the development of environmentally friendly CRF using biological macromolecules/polymers (carbohydrates, lignin, etc.) has emerged.[27,28] Compared to synthetic polymers, biological macromolecules are relatively inexpensive,[29] biodegradable, biocompatible, and nontoxic and contribute to improving soil properties.[30,31] In addition, biological polymers appear to be a potential alternative to synthetic polymers for CRF fertilizer coating and could contribute significantly to organic waste recycling and the circular economy. However, the release of nutrients also depends on the structure and nature of biological macromolecules, the thickness of the coating layer,[32] its homogeneity,[27] and the imperfections in the coating surface,[33,34] such as pinholes and cracks. In recent years, some biopolymers have been studied as CRF coating fertilizers, i.e., lignin,[10] k-carrageenan,[27] chitosan,[35] and alginates.[36] Lignin (L) is a cheap and natural polymer with remarkable properties that is abundantly available as a waste material, as it is recovered mainly as a byproduct from wood pulping processes, with approximately 100 million tons produced annually worldwide.[37] Moreover, compared to other polymers, lignin is a renewable, biodegradable, amorphous, relatively hydrophobic biopolymer that is rich in carbon, which could contribute to increasing the soil organic matter content.[11] However, some studies of lignin-CRF coating were mostly performed using only commercial lignins.[10] Garcia et al. used a commercial kraft pine lignin mixed with rosins and in some cases linseed oil to coat urea[11] and triple superphosphate (TSP)[10] fertilizers. They showed that coated TSP with a thickness of 83−106 μm released less than 20% of P after 3 days, while uncoated TSP released the totality of its P within the same duration. For coated urea, the use of rosins and linseed oil as well as lignin in a coating formulation increased the efficiency of this fertilizer. Mulder et al.[38] found that coating urea fertilizer with soda flax lignin and alkenyl succinic anhydride as an additive significantly decreased the release of urea in water. Therefore, the properties of extracted lignin macromolecules (origin, chemical structure, molecular mass, etc.) as a coating agent need to be evaluated and compared to those of commercial lignin, synthetic polymers, and some carbohydrates. k-Carrageenan (C) is another interesting biopolymer extracted from certain species of red seaweeds (Rhodophyta).[39] The biopolymer k-carrageenan is a hydrophilic linear sulfated galactan with a high water absorption capacity.[27] Wan et al.[27] reported that k-carrageenan-Na-alginate and k-carrageenan-*g*-poly(acrylic acid)/Celite formulation composite superabsorbents were used as inner and outer coating materials, respectively, for nitrogen fertilizer. This double-coated fertilizer had a slow-release behavior and improved the water-holding capacity and water-retention properties of the soil. In most cases, plasticizers are added to the film-forming polymer to improve the mechanical properties of the coating shell. Some of the plasticizers used in the literature are glycerol, Lupranol, Acronal, styronal, sorbitol, polyethylene glycol (PEG) 400, PEG 2000, PEG 6000, dibutyl sebacate, dibutyl phthalate, triacetin, and glycerine.[38,40−43]

The objectives of the present study were to (i) develop a process for coating TSP with lignin extracted from olive pomace (OP) biomass and k-carrageenan; (ii) prepare different lignin-k-carrageenan formulation composites and evaluate the impact of their properties on TSP phosphorus release; and finally (iii) evaluate the impact of plasticizer addition (PEG 2000) on lignin-k-carrageenan formulation properties and phosphorus release.

EXPERIMENTAL SECTION

In this study, olive pomace (OP) was used as a starting material for lignin extraction. OP was provided from a Moroccan olive press (Tadla region). Kappa carrageenan (CAS: 1114-20-8), polyethylene glycol (Mw = 2000 g/mol; CAS: 25322-68-3), calcium chloride ($CaCl_2$, CAS: 10043-52-4), potassium carbonate (K_2CO_3, CAS: 584-08-7), sodium bromide (NaBr, CAS: 7647-15-6), and sodium hydroxide (NaOH, CAS: 1310-73-2) were purchased from Sigma-Aldrich. Triple superphosphate (TSP), a granular phosphate fertilizer (46% P_2O_5), was produced and offered by OCP Group, Morocco.

Lignin Polymer Extraction from Olive Pomace (OP) Biomass. The lignin polymer used in this study was extracted from OP biomass using the alkali method. OP biomass was ground with knife milling (Retsch SM100) using a screen size of 1 mm. A total of 200 g of ground OP biomass was immersed in 1.5 L of water with 0.16 M NaOH. The mixture was reacted in a beaker and maintained at 70 °C with stirring (300 rpm) for 2 h using an adapted method according to El Miri et al.[44] The concentrated alkaline solution was separated by centrifugation (10 min, 4000 rpm). The concentrated black liquor containing lignin was used directly for coating formulation and film composite preparation. For lignin polymer characterization, lignin was recovered after precipitation with HCl (pH = 2−3) of some concentrated black liquor.

Chemical Analysis. C, H, N, and S measurements for OP and lignin were performed by elemental analyses (Analyzer Vario MICRO v4.0.2, France). The chemical composition of OP was determined by a high-performance liquid chromatography (HPLC) system equipped with a column (HPX-87H, BioRad, USA) and a refractometer detector at 40 °C using 0.005 M H_2SO_4 as the eluent with a flow rate of 0.3 mL/min. The first step was acid hydrolysis. This procedure was carried out on crushed biomass (<1 mm). After sulfuric acid attack, the obtained suspension was filtered. The soluble phase was injected on the HPLC system for sugar content determination (glycose, xylose, and arabinose) and then calculation of percent cellulose and percent hemicellulose using these equations:[45,46]

$$\text{cellulose}\left(\frac{\text{g}}{\text{100 g of sample}}\right) = \frac{\text{glucose}\left(\frac{\text{g}}{\text{L}}\right) \times V_{\text{tot}}}{M_{\text{ini}} \times 1.11} \quad (1)$$

$$\text{hemicellulose}\left(\frac{\text{g}}{\text{100 g of sample}}\right) = \frac{V_{\text{tot}}\left(\text{xylose}\left(\frac{\text{g}}{\text{L}}\right) + \text{arabinose}\left(\frac{\text{g}}{\text{L}}\right)\right)}{M_{\text{ini}} \times 1.13} \quad (2)$$

where V_{tot} is the total volume of ultrapure water, M_{ini} is the initial weight of the biomass (<1 mm), 1.11 is the conversion factor between glycose and cellulose, and 1.13 is the conversion factor between monomers (xylose, arabinose) and cellulose. After that, the remaining solid phase was lignin. It was dried at 105 °C and weighed, and percent lignin was calculated. Three samples were characterized, and the reported results are average values.

FTIR and TGA Analysis. The extracted lignin and different formulation composites were analyzed using Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). FTIR was performed on a Tensor 27 apparatus equipped with ATR accessory. The experiments were carried out in the 4000−400 cm^{-1} region with a resolution of 4 cm^{-1} and an accumulation of 16 scans. The FTIR spectra were acquired in absorbance mode. TGA was conducted under nitrogen (with a flow rate of 50 mL/min) using a TGA instrument (Mettler Toledo) with a 5 °C/min heating rate from 25 to 900 °C. Ash content was determined under air (with a flow rate of 50 mL/min) with an isothermal segment (900 °C for 1 h).

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Preparation of Formulation Composites (Films). Formulations and film composites were prepared using k-carrageenan (C), lignin (L) solution, and polyethylene glycol 2000 (PEG) in different ratios (Table 1). Black liquor (33.34 g lignin/L) obtained after alkali treatment of OP was used directly without stirring. Carrageenan solution (C) was prepared (0.5 w/w%) under constant stirring for 2 h. The LC-based composite was prepared as follows, where 80% lignin was mixed with 20% k-carrageenan (w/w). The LC-PEG-based composite was also prepared similarly to the LC composite, except for the addition of 30% PEG to the mixture. All formulations were stirred overnight at room temperature. The same formulations were used for film composite preparation and TSP coating. For the film preparation, the mixtures were deposited onto square Petri dishes (12 cm), and the water was evaporated by drying overnight at 40 °C.

Table 1. Composition of Different Prepared Formulations

polymers-based formulation	lignin (%)	carrageenan (%)	PEG 2000 (%)
lignin (L)	100	0	0
carrageenan (C)	0	100	0
LC	80	20	0
LC-PEG	55	15	30

Characterization of Lignin-Carrageenan Formulation Film Composites. *Water Solubility.* The weight loss of the film composites was monitored for 48 h. The weighted dried films M_0 (approximately 20−50 mg) were placed in Eppendorf tubes, and 1 mL of distilled water was added. The solutions were incubated (5 min, 0.5 h, 1 h, 2 h, 6 h, 8 h, 24 h, 32 h, and 48 h). After each interval, the mixtures were centrifuged at 4000 rpm for 5 min. The supernatants were removed, and the residue was dried and weighed (M_s). The remaining mass from the film composites was calculated using eq 3. All the determinations reported here are triplicate results.

$$W = \frac{M_s}{M_0} \times 100 \quad (3)$$

Contact Angle Measurements (CA). The hydrophobicity of the film composites was evaluated by analyzing the behavior of water drops injected on their surface. Before contact angle measurements, films were cut into small rectangles (0.5 cm × 2 cm), and their support sides were glued to glass slides using double-sided tape. Samples were equilibrated for 5 days at 35%, 46%, or 60% relative humidity (RH) in desiccators in the presence of $CaCl_2$-, K_2CO_3-, and NaBr-saturated solutions, respectively. A humidity detector was used to verify the obtained humidity. Contact angle measurements were realized with a goniometer (Digidrop, GBX, France) equipped with a diffuse light source and a CCD camera (25 frames/sec). A droplet of ultrapure water (~3 μL) was deposited on the film surface with a precision syringe (Teflon needle, 0.82 mm external diameter). The method is based on image processing and curve fitting for the contact angle. The video was analyzed frame-by-frame with GBX software to determine the contact angle as a function of time.[47,48] Three measurements were performed on each sample.

Mechanical Properties Measurements. The film elasticity (tensile modulus E), tensile strength (σ_s), and elongation at break (ε_b) were studied using tensile tests. Tests were performed on films using a texture analyzer (TA, XT plus). The tensile specimens were cut into rectangles (80 mm in length and 10 mm in width). The gauge length was fixed at 30 mm, and the speed of the moving clamp was 5 mm/min.[49] Measurements were carried out at room temperature. At least three samples were characterized, and the reported results are average values.

Preparation and Characterization of Coating TSP Fertilizers. Granules of TSP fertilizer (50 g) were sieved to select homogeneous granules with diameters of 2−3 mm and then placed into a rotary drum (12 rpm, capacity of 11 L) developed in our laboratory (Figure 1). The distance between the spray nozzle and the center of the rotary drum was 25 cm. The, 50 g of TSP granules was covered with a layer of different formulations (3 g) based on lignin and carrageenan by spraying at regular time intervals. Then, the coated TSP granules were continuously dried in the rotary drum by hot air stream (65 °C).

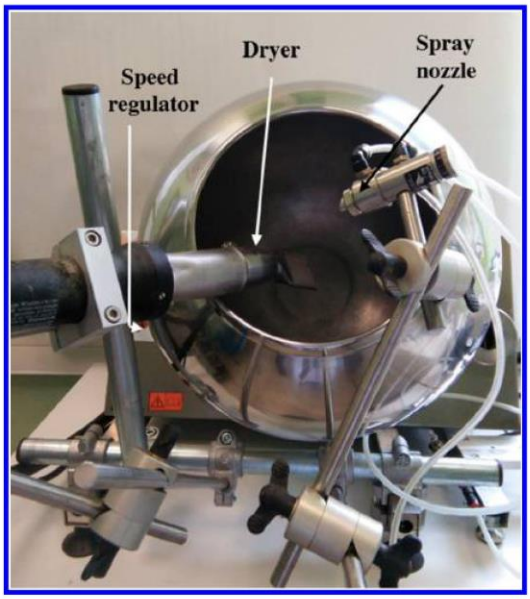

Figure 1. Rotary drum for coatings developed in this study.

Morphology and Thickness Measurement of Coated TSP. The morphology of the coated TSP was evaluated by a tabletop scanning electron microscope (SEM) (Phenom ProX, Phenom-World) using a backscattered electron detector (acceleration voltage of 10 kV, mode image). Three granules of each type of coated TSP fertilizer were randomly chosen. These granules were cut in half with a razor blade and fixed on a support. For thickness measurements of coating layers, the drawing rule option of SEM was used, and three measurements of different areas on each granule were performed.

Water Absorbency of Coated TSP. Coated TSP granules were dried at 50 °C in a vacuum oven in the presence of P_2O_5. Samples were weighed to a constant weight (complete drying). Then, they were conditioned in desiccators at three relative humidities, i.e., 35%, 60%, and 80% in the presence of $CaCl_2$-, NaBr-, and KCl-saturated solutions, respectively. The water absorbency of coated TSP was monitored for 3 days.[10] A humidity detector was used to verify the humidity in the desiccators. Samples were weighed after each 24 h, and the absorbed water was determined by the weight difference between dried and conditioned samples. All the determinations reported here are triplicate results.

Slow-Release Behavior of Coated TSP in Water. For release experiments, uncoated and coated fertilizers were equilibrated in a desiccator for 3 days at 60% RH in the presence of NaBr-saturated solution. Then, 0.25 g of each type of coated TSP was immersed in 50 mL of distilled water in glass bottles. The bottles were conditioned at a constant temperature of 25 °C. After 15 min, 1 h, 6 h, and 1, 2, 3, 4, and 5 days, 1 mL samples of different solutions were sampled for phosphorus determination, and an additional 1 mL of distilled water was added to the bottle to maintain a constant volume. All the release experiments were carried out in triplicate. The phosphorus concentration was determined using the colorimetric molybdenum vanadate method.[12] The phosphorus release at each time was obtained by eq 4 proposed by Rashidzadeh et al.[50] and expressed in relation to the phosphorus concentration and total weight of phosphorus contained in the TSP fertilizer. All the determinations reported here are triplicate results.

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Table 2. Chemical Analysis of Olive Pomace and Extracted Lignin (n = 2)[a]

	C%	H%	N%	S%	O%
OP	51.02 ± 0.11 a	6.85 ± 0.14 a	0.71 ± 0 a	0.08 ± 0 a	36.38 ± 0.25 a
lignin	58.24 ± 0.00 b	7.89 ± 0.03 a	1.79 ± 0.01 b	0.18 ± 0.01 a	28.05 ± 0.07 b

[a]Within a column, means followed by the same letter are not significantly different at $p < 0.05$

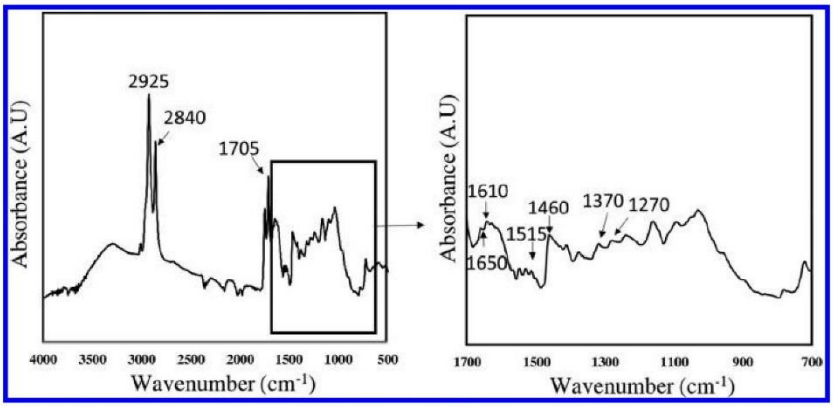

Figure 2. FTIR spectra of alkali lignin extracted from OP.

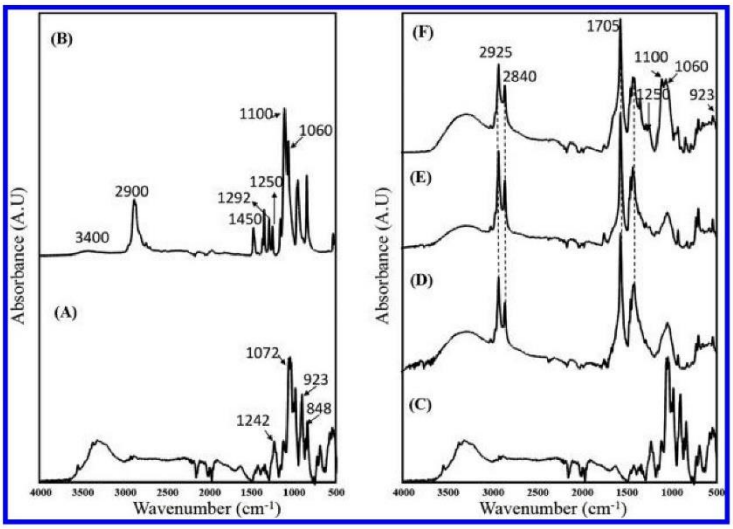

Figure 3. FTIR spectra of (A) k-carrageenan powder, (B) PEG 2000 powder, (C) k-carrageenan film, (D) lignin film, (E) LC-film, and (F) LC-PEG film.

$$\mathrm{CR}\ (\%\mathrm{w/w}) = \frac{V_e \sum \mathrm{Cp}_i + V_0 \mathrm{Cp}_n}{\mathrm{mp}_0} \times 100 \quad (4)$$

where CR is the cumulative amount of phosphorus release (%) from the TSP fertilizer, V_e is the sampling volume, V_0 is the initial volume of release media, Cp_i and Cp_n are the phosphorus concentrations (mg/mL), i and n are the sampling times, and mp_0 is the total weight of phosphorus contained in the TSP fertilizer.

Data Analyses. The average value was calculated for each treatment. Analysis of variance (ANOVA) among treatments was performed using R version 3.4.2. The effect of relative humidity and formulation on contact angle; the effect of relative humidity, formulation, and time on water absorbency; and the effect of formulation and time on phosphorus release were tested by two-way ANOVA. One-way ANOVA was performed to analyze the effect of formulation on the Young's modulus (E), tensile strength (σ_s), elongation at break (ε_b), and thickness of the coating agent. If significant, a Tukey post hoc test was used for pairwise multiple comparisons ($p < 0.05$).

RESULTS AND DISCUSSION

Olive Pomace (OP) and Lignin Characterization. Compared to wood and other lignocellulosic biomass, olive pomace (OP) is rich in lignin (33.2% ± 2.22 a),[51] while its contents of hemicellulose, cellulose, and ash were estimated to be (10.29% ± 0.02 b), (14.8% ± 0.43 b), and (4.95%), respectively. The elementary composition of OP biomass (Table 2) was estimated to be 51% C, and the C/N ratio was 71.85. The alkali-extracted OP lignin contained more C, H, N, and S than the raw material and was comparable to alkali-extracted lignin from Masson's pine sulfate pulping liquor.[52]

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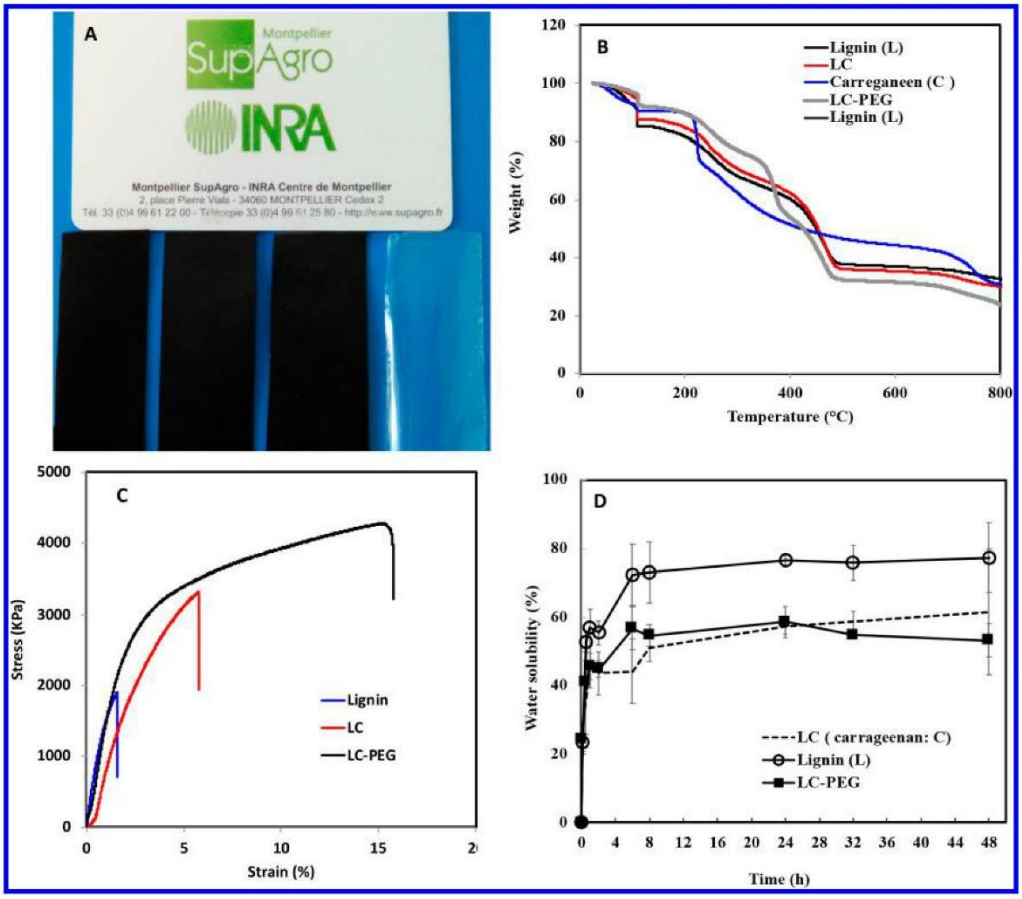

Figure 4. (A) Photograph of film composites. (B) TGA, (C) mechanical properties, and (D) solubility in water of different film composites based on lignin (L), k-carrageenan (C), and PEG.

FTIR spectra (Figure 2) show two intense bands at 2925 and 2840 cm^{-1} related to the C−H stretching vibration in aliphatic structures and to the symmetrical CH stretching vibrations in $-CH_2$, respectively, both of which are attributed to fatty acids.[53] The identified bands at 1610, 1515, and 1460 cm^{-1} correspond to aromatic ring vibrations, and the bands at 1705 and 1650 cm^{-1} can be attributed to non-conjugated and conjugated carbonyl groups, respectively.[54] Lignin-guaiacyl was identified at 1270 cm^{-1}, and lignin-syringyl was identified at 1370 cm^{-1}. The extracted OP lignin showed a typical FTIR spectra of guaiacyl-syringyl lignin in agreement with reports by Xiao-Xia[52] and Gutierrez.[54]

Characterization of Lignin-Carrageenan-Based Composites. *FTIR and TGA Analysis.* The identified bands at 1242, 1072, 923, and 848 cm^{-1} (Figure 3A) were assigned respectively to the sulfate group, glycosidic linkage, 3,6-anhydrogalactose, and galactose-4-sulfate of k-carrageenan.[55] FTIR analysis of PEG 2000 (Figure 3B) shows several specific peaks, i.e., a peak at 3400 cm^{-1} corresponding to O−H stretching of the hydroxyl group, a peak at 2900 cm^{-1} corresponding to C−H stretching of alkanes, a peak at 1450−1292 cm^{-1} corresponding to C−H scissoring and bending, a peak at 1250 cm^{-1} corresponding to C−O stretching of the alcohol group, and a peak at 1100−1060 cm^{-1} corresponding to the C−O−C ether group.[56]

The spectrum of the carrageenan film (Figure 3C) shows the same peaks as k-carrageenan powder with identified bands at 1242, 1072, 923, and 848 cm^{-1}. The lignin film (Figure 3D) also shows the same bands of lignin polymer at 2925, 2840, 1705, 1650 cm^{-1}, etc. as discussed previously. For LC and LC-PEG film composites, characteristic bands of lignin (2925, 2850, 1705 cm^{-1}), carrageenan (923 cm^{-1}), and PEG (1060, 1100, 1250 cm^{-1}) were all identified (Figure 3E and F).

Figure 4A shows the appearance of different prepared films with lignin and carrageenan. Figure 4B presents the TGA results of different films. Figure 4B shows that the thermal degradation of lignin and the LC film composites was similar and was very different from that of carrageenan and the LC-PEG film composites. Generally, the different film composites showed two major degradation steps, i.e., water desorption in the first range of 25−200 °C and a major decomposition step in the range of 200−400 °C. All the samples showed losses in the first step (25−200 °C) ranging from 3−13%. The weight loss in the first step is mainly associated with the bound and free water, but above 150 °C, the breaking of some bonds in OH groups gradually occurs. Comparing all samples in the first range of 0−200 °C allowed observation of the loss of moisture content, which was the highest for lignin (9.12%), followed by carrageenan (7.36%) and the LC-based composite (4.89%), whereas the LC-PEG sample had the lowest moisture of only

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3.45%. However, the sample with the largest weight loss in the range of 200−400 °C was carrageenan, followed by lignin, and the lowest weight loss being that of the LC-PEG-based composite. This mass is predominantly associated with inorganic material (such as silicates and carbonates) but can still contain carbon, which is also referred to as fixed carbon. Another reason for the low loss of original material lies in the stability of the LC-PEG samples in the interval of 200−400 °C, exhibiting the lowest decrease among all samples, most likely due to the presence of PEG.

Mechanical Properties. The k-carrageenan (C) polymer formed a brittle film that was impossible to cut without damage; as a consequence, tensile tests were not performed on it. This observation was confirmed by Cazon et al, who reported that polysaccharide films are usually brittle.[57] Figure 4C and Table 3 show the tensile strength (σ_s), elongation at break (ε_b), and tensile modulus (E) of different film composites, which depend on the degree of cross-linking in the presence of PEG as a plasticizer. Table 3 clearly shows a significant difference in tensile strength (σ_s) and elongation at break (ε_b) between different film composites ($p < 0.05$), while no difference was observed in the tensile modulus (E). The σ_s and ε_b of the film composites varied between 1135 and 4296 kPa and 1.46% and 16.65%, respectively. Among all samples, LC-PEG exhibited the highest σ_s and ε_b values, while the lignin film composite control displayed the lowest σ_s and ε_b values (Table 3, Figure 4C). Compared to that of the lignin film polymer, the σ_s values of the LC and LC-PEG film composites increased by 224% and 279%, respectively. Moreover, an increase in ε_b of approximately 542% and 1041% was also observed for the LC and LC-PEG films compared to the lignin film, respectively. The increase in elongation for the LC and LC-PEG films compared to the lignin film could be explained by the hygroscopicity of the carrageenan polymer and the interaction of the LC matrix with PEG.[58] Table 3 and Figure 4C also show that compared with the LC film, the LC-PEG film shows an increase in σ_s because of the addition of PEG (MW 2000 g/mol). This finding implied that PEG could make LC-PEG film composites more flexible. Aadil et al.[59] reported that PEG increased intermolecular space by reducing the hydrogen bonding interaction between polymers. This result is also in accordance with the study by Cao et al.,[60] who suggested that using PEG could increase the σ_s of polysaccharide film composites. Aadil et al.[59] used lignin (L) extracted from acacia wood, alginate (A), and PEG 4000 for LA and LA-PEG composite preparation (L/A ratio = 1/4). The authors reported that LA-PEG film composites had a high σ_s of 569 kPa compared to 413 kPa for LA. In the presence of

Table 3. Tensile Modulus (E), Tensile Strength (σ_s), and Elongation at Break (ε_b) of Lignin (L), LC, and LC-PEG (n = 3)[a]

	E (kPa)	σ_s (kPa)	ε_b (%)
L	787 ± 385 a	1135 ± 766 a	1.46 ± 0.11 a
LC	1191 ± 356 a	3674 ± 318 b	9.37 ± 1.99 ab
LC-PEG	1276 ± 304 a	4296 ± 161 b	16.65 ± 4.40 b

[a]Within a column, means followed by the same letter are not significantly different at $p < 0.05$.

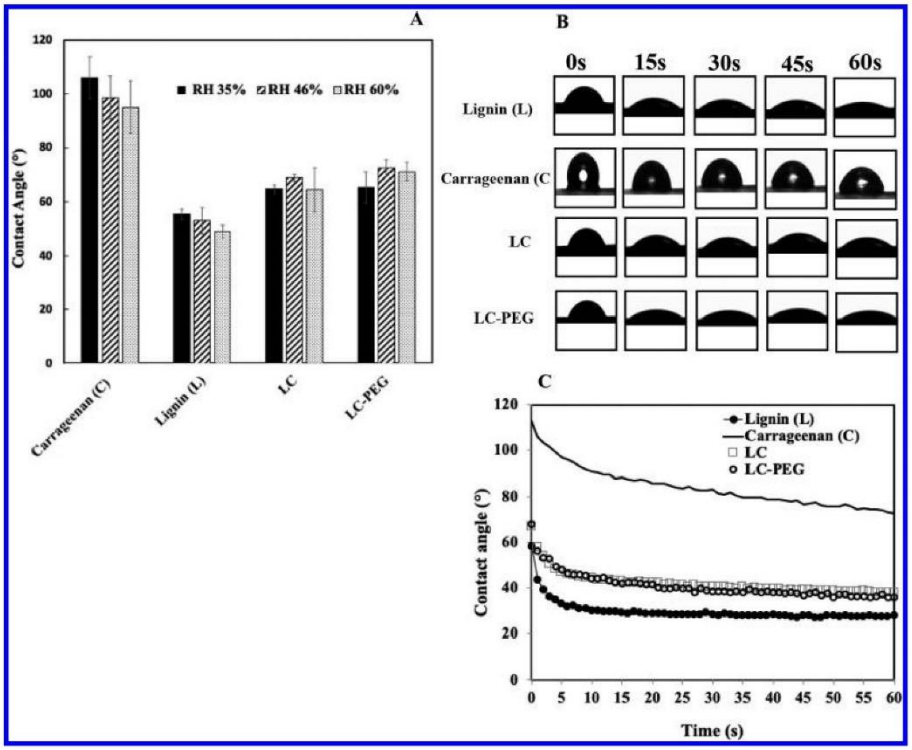

Figure 5. (A) Contact angle measurements (n = 3) of films at different RH values (35%, 46%, and 60%). (B) Water drop behavior over time at 35% RH and (C) contact angle behavior over time at 35% RH.

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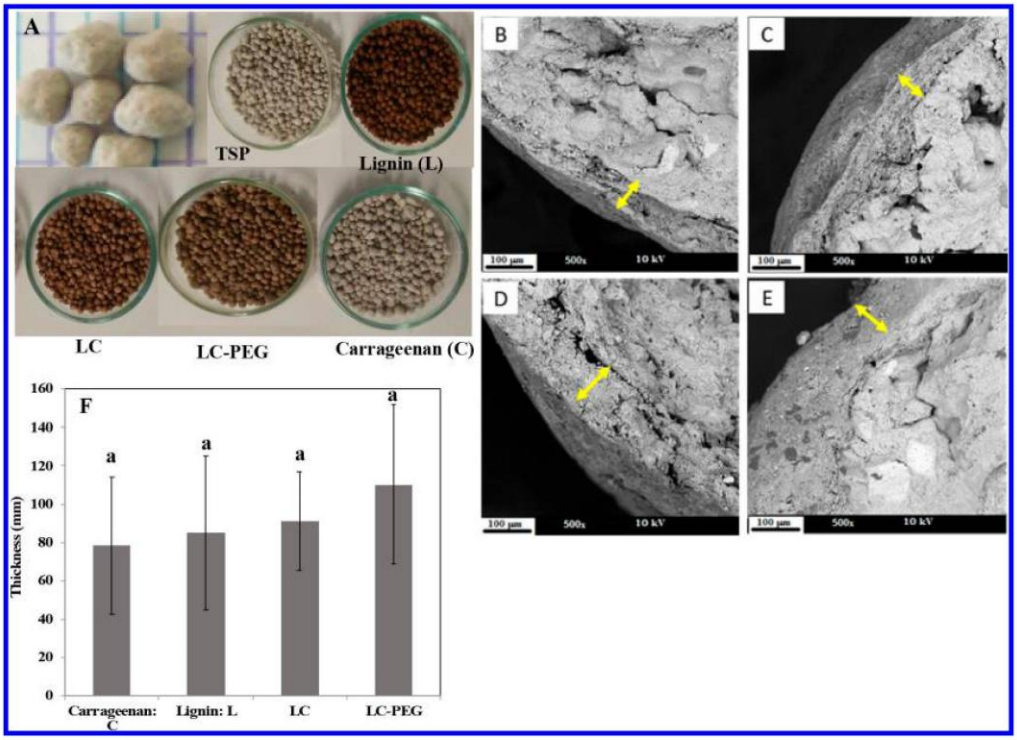

Figure 6. (A) Real image of noncoated and coated TSP and cross-sectional SEM images of TSP fertilizers with (B) carrageenan, (C) lignin, (D) LC, and (E) LC-PEG. (F) Thickness of coating layers (n = 9).

PEG, lignin interacted with alginate by the formation of hydrogen bonds that replaced polymer−polymer interactions and impeded the formation of polymer−water hydrogen bonds in amorphous region.[59] In comparison, the LC and LC-PEG composites (this study) have higher σ_s values than those of LA and LA-PEG.[59] This result is probably due to the higher lignin content in the LC formulation composite (L/C ratio of 4/1) than in the LA composite (L/A ratio of 1/4). In addition, this difference in σ_s also depends on lignin structure, polysaccharide properties (carrageenan compared to alginate), polymer−polymer interactions, and film thickness. Figure 4C clearly indicates the presence of an elastic zone in lignin and the LC and LC-PEG composites, which was not significantly different among the different formulations. Elasticity is an important parameter for the water absorbency of the coating polymer.[61] In comparison, the LC-PEG composite was characterized by an additional plastic zone and a higher ε_b than those of the other composites (Figure 4C). The elasticity and plasticity give the film the capacity to extend before breaking.[62] This property could be important for a coating formulation to resist pressure without breaking during the swelling of a coated granule.[15] The blending of lignin with carrageenan in the presence of PEG led to enhanced tensile properties. Indeed, the mechanical properties of different formulation composites are classified in the order of LC-PEG > LC > lignin. The high Young's modulus (E), high tensile strength (σ_s), and high elongation at break (ε_b), along with plastic behavior, could be interesting for CRF coating formulation properties.

Water Solubility. To make a good CRF coating, knowledge of the water solubility of the film is essential. The carrageenan film (0.5 w/w%) formed a gel in water, making it difficult to measure its dissolution in water. The results showed that the solubility after 32 h of incubation of LC blended films in water ranged between 54.90% and 75.96% in the order of lignin > LC > LC-PEG (Figure 4D). The high solubility of the lignin film could be explained by the presence of sodium ions (Na^+) at the surface of the films (lignin extracted with NaOH and without HCl precipitation) and a permanent ion-exchange between H^+ of water and Na^+.[63] The low solubility of LC compared to the lignin film is possibly due to the polar SO_4^- side chain groups of carrageenan that bind to lignin (ONa^+) molecules.[64] This effect resulted in reduced exposure of the hydrophilic groups of carrageenan and hydrophobic groups of lignin to water molecules, which led to a stable and homogeneous composite. The LC film composite plasticized with PEG had less water solubility than that of the LC and lignin formulations, which is most likely due to the low degree of hydrogen bonding of LC in the presence of PEG. This result was in accordance with research by Aadil et al.,[59] who reported that the blending of lignin with alginate in the presence of plasticizers significantly decreased film solubility. LC-PEG film composites with low water solubility could be used as an excellent CRF coating formulation.

Surface Properties. The contact angles of different film composites of lignin (L), carrageenan (C), LC, and LC-PEG under different relative humidity (RH) conditions were measured (Figure 5A). Figure 5B shows an example of a water droplet on different films from which the contact angle was determined. Significant differences were observed between different film composites ($p < 0.05$). No effect of RH on the measured contact angle was observed ($p > 0.05$) (Figure 5A).

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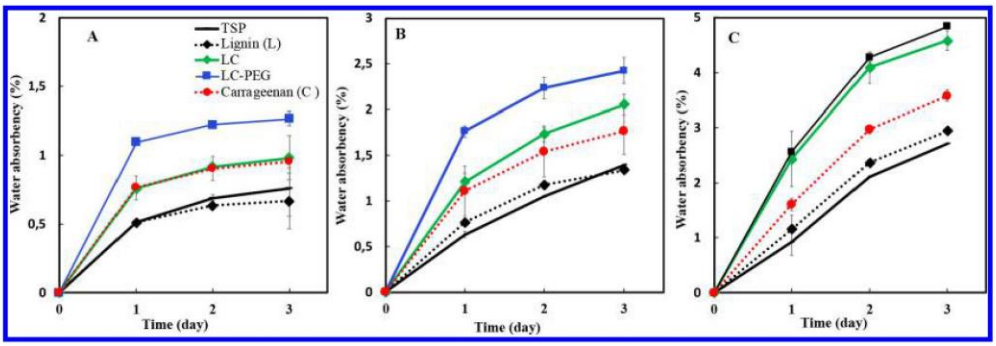

Figure 7. Water absorbency as a function of the time at different RH values: (A) 35%, (B) 60%, and (C) 80% (n = 3).

The results showed that the contact angle of the LC blended films ranged between 49° and 105° in the order of carrageenan > LC-PEG = LC > lignin (Figure 5A). The lignin film composite had a lower contact angle than LC and LC-PEG. It is reasonable to assume that these lignin-Na^+ surfaces had a high prevalence of polar groups, particularly hydroxyl groups, due to the present method of isolation/extraction. Notley et al.[65] reported that the contact angles of films of softwood kraft lignin, softwood milled wood lignin, and hardwood milled wood lignin were 46°, 52.5°, and 55.5°, respectively. Norgren[63] also showed that lignin films of softwood lignin isolated from the kraft process had a contact angle of 46°, in agreement with our results. The effect of the lignin extraction method (alkaline, organosolv, etc.) and origin (wood, gramineous, etc.) on the water contact angle on lignin thin films is currently under investigation. Compared to the lignin and LC-PEG films, the carrageenan films had the highest contact angle of approximately 95−105°, which is probably due to the strong intramolecular hydrogen bonding beneath the film surface.[48] Karbowiak[48] and Jayasekara[66] also observed this phenomenon with i-carrageenan and starch films. The addition of carrageenan to the lignin formulation (1/4 ratio) increased the contact angle from 49° to 55.4° to 64.5−69°. However, no effect of PEG addition on the measured contact angle was observed. Karbowiak et al.[48] reported that the addition of plasticizer could affect the structure and composition of the surface of both film composites, which depend on the plasticizer nature and content. In this study, the effect of PEG on the contact angle is probably masked by the high lignin content present in the LC-PEG composite. The contact angle of different film composites was also measured as a function of time (see Figure 5C). The contact angle was relatively stable; however, it decreased slightly during the next 60 s. This decrease is due to evaporation and absorption.[48] As the water evaporates, the contact angle decreases due to pinning of the droplet. It is also possible that some minor swelling and absorption of the film, which depend on the hydrophobicity of the film composite, contribute to this observed decrease (Figure 5C). This phenomenon was also observed with kraft lignin by Norgren et al.[63]

Coated TSP Fertilizer Properties. *Physicochemical and Morphological Characterization of Coated TSP Fertilizers.* Figure 6A presents a visual aspect of the coated TSP fertilizer granules compared to uncoated TSP, which clearly indicates that TSP granules were completely covered by the film coating. The visual aspect of the carrageenan-coated TSP fertilizer was similar to that of uncoated TSP (carrageenan solution was colorless), while the granules coated by lignin-based formulations were brown. The microscopic structures of the coated TSPs were also obtained by using scanning electron microscopy (SEM), as shown in Figure 6B−E. Figure 6B−E, which present cross sections of coated TSP fertilizers, show that the coating film had a compact and porous structure. The border and adhesion between TSP and the film coating was irregular and difficult to observe, most likely due to the nonspherical shape and irregular surface of the initial TSP granules (Figure 6A).

The thicknesses of different coated TSP granules were also determined (Figure 6F) and were found to not be significantly different (p > 0.05). The results showed that the thickness of different coated TSP granules ranged between 25 and 170 μm. The thickness of the coating is an important parameter that can significantly control nutrient release.[12,32] Ahmad et al.[32] showed that a high thickness resulted in a low phosphate release rate due to the formation of a long resistance path, which hinders the diffusion of P. They also showed that within 10 days, coated pellets with a thickness of 63 μm released 325 g P/m^3, while the release with a thickness of 128 μm was 225 g P/m^3. Jarosiewicz[12] also showed that the release rate can be controlled by adjusting the thickness of the coating.

NPK granules coated with one layer of 17% polyacrylonitrile (thickness ≈ 0.2 mm) released 93.7% K^+ within 5 h, while granules with three layers of the same formulation (thickness ≈ 0.49 mm) released only 11.7%. The effect of the thickness and porosity of TSP fertilizers coated by lignin and some polysaccharides on the phosphorus release in water and soil is currently under investigation. The water absorbency of different film composites was also measured as a function of time and relative humidity (RH) (see Figure 7). For the slow-release fertilizers, the high water absorbency of the coating formulations is useful. The time required to reach maximum water absorbency of different formulations at 35%, 60%, and 80% RH was studied and fixed to 3 days (Figure 7). As can also be seen from Figure 7, the magnitude of the effect of RH on the water absorbency of coated TSP fertilizers increased over time.

According to Liang,[61] the water absorbency of a super-absorbent polymer depends on the content of hydrophilic groups, cross-link density, polymer network behavior and elasticity, type of solvent, ionic strength of the external solution, etc. For example, the water absorbency at 80% RH (3 days) was found to be significantly higher in the LC-PEG (4.84%) and LC (4.55%) film composites than in TSP (2.71%), lignin (2.94%), and carrageenan (3.58%). The high

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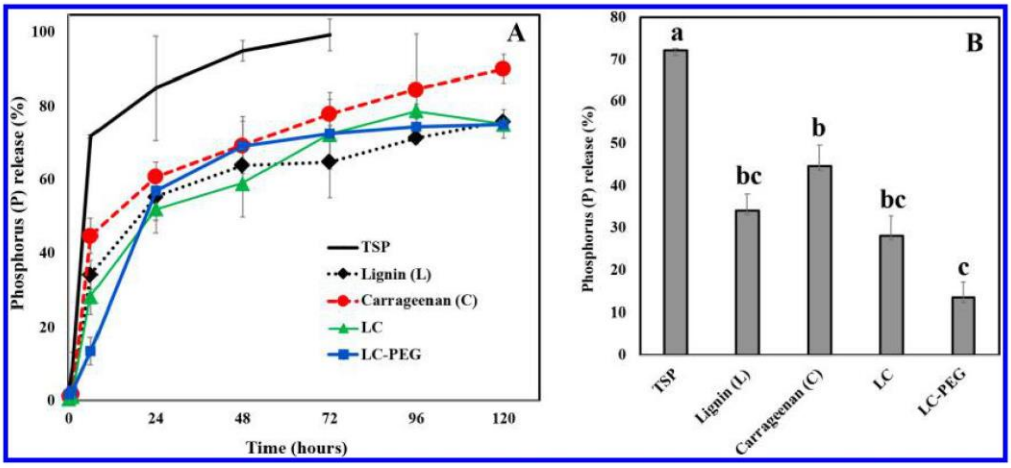

Figure 8. Release of phosphorus of TSP and coated TSP fertilizers in water: (A) kinetics for 120 h and (B) for 6 h.

water absorbency of the LC-PEG and LC film composites might be due to the low degree of cross-linking between the lignin and carrageenan molecules in the presence of PEG. The lower water absorbency of lignin might be due to the hydrophobic nature of lignin molecules, allowing less water to be absorbed.[63] Indeed, the elastic properties of LC-PEG were significantly higher than those of the other film composites in the order of LC-PEG > LC > lignin, which might also explain the high water absorbency of LC-PEG. Furthermore, high water absorbency is one of the greatest properties of coating release fertilizers that are used in agriculture, i.e., a coating with high water absorbency could absorb more water from rain or irrigation. Therefore, the coated mineral fertilizer with high swelling and water absorbency capacity and slow-release behavior could be more effective in agriculture and sustainable chemistry of P.[61]

Slow Release of Phosphorus from Coated and Uncoated TSP Fertilizers. The trend of P release from TSP and different coating formulations could be observed in Figure 8. Among the fertilizers, TSP showed the highest phosphorus (P) release, with more than 72.0% ± 0.42 and 95.06% ± 4.28 P released within 6 and 48 h, respectively, and P was completely dissolved after 72 h (Figure 8A). The time required to reach maximum (P) release from different formulations was studied and achieved within 72 h (Figure 8A). LC with or without PEG and the lignin formulations exhibited the slowest P release. The amounts of phosphorus released at 6 h (Figure 8B) from the lignin@TSP (34.28% ± 3.95) and LC@TSP (28.22% ± 4.81) formulations were not significantly different. By contrast, LC-PEG@TSP (13.51% ± 3.68) had the lowest amount of P released, and carrageenan@TSP (44.89% ± 3.68) had the highest other than 72.0% for TSP. For the release behaviors of P, all the curves showed similar release amounts, which were approximately 100% for TSP, 78.12% for carrageenan@TSP, 71.66% for LC@TSP, 70.46% for LC-PEG@TSP, and 65.0% for lignin@TSP after 3 days. The presence of lignin had considerable effects on the release behaviors of P from LC formulations, which is most likely due to the hydrophobic properties and low porosity of the lignin polymer compared to carrageenan. The slow-release behavior of P from LC@TSP and LC-PEG@TSP can be related to the high elasticity, high tensile strength, and high elongation at break of the composites, which could help the membrane resist pressure.[15] In addition, the hydrophobicity and low solubility in water of the LC@TSP and LC-PEG@TSP formulations endow them with more resistance in water; consequently, the amount of P released is decreased.

However, due to the recalcitrance of lignin to degradation in soil, dissolution tests of lignin-coated TSP in the soil matrix are necessary to evaluate the rate of P release in soil. The effect of lignin structure, thickness, porosity (alkaline, organosolv, etc.), and origin (wood, gramineous, etc.) on the release behaviors of P in water and soil is currently under investigation. Garcia et al.[10] used a commercial kraft pine lignin, rosins, and, in some cases, linseed oil for TSP fertilizer coating. They showed that coated TSP with a thickness of 83−106 μm released less than 20% P after 3 days. In comparison, lignin@TSP, LC@TSP, and LC-PEG@TSP fertilizers released approximately 65−78% within the same duration, which can be attributed to the presence of a high amount of rosins. According to previous studies,[12,13,15,17,61,67] the release behaviors of P depend strongly on the nature and amount of polymer, cross-link density, polymer network behavior and elasticity, thickness, porosity, water absorbency, and coating preparation method. For these reasons, it is very difficult to compare different studies in the literature. Once the coated fertilizer is in the soil, the degradation is also a parameter that influences the release behavior.[15] A very rapid biodegradability of coating agent in soil is undesirable because it will accelerate the fertilizer release, but a nonbiodegradable material is undesirable too (accumulation of residuals in soil). Carrageenan is a high biodegradable polysaccharide.[62] Lignin is used also to reinforce polysaccharides and to decrease their weight loss during the burial soil test.[68] Majeed et al.[68] reported that the lignin reinforcement of urea-cross-linked starch film reduced the starch biodegradability and slow the release of nitrogen in aerobic soil condition. The combination of carrageenan and lignin, developed in this work, could be a good way to slow the biodegradability in the soil until the total nutrients release occurred. However, a deep study is occurred to evaluate the biodegradability of lignin-carrageenan in the soil, in the absence or presence of polyethylene glycol.

■ CONCLUSION

The objectives of this study were to investigate the possibility of coating TSP fertilizer with recycled materials using lignin

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extracted from OP biomass and to evaluate the influence of plasticizer addition on lignin-polysaccharide-based film properties. The results showed that more than 72% and 84% P was released from uncoated TSP within 6 and 24 h, respectively, and that the amount of P released reached 100% within 72 h. By contrast, the amount of P released from formulations with lignin and additives (carrageenan and PEG) decreased to 13.5−44.8%, 52−61%, and 65−78% within 6, 24, and 72 h, respectively. Within 6 h, LC-PEG@TSP (13.51% ± 3.68) and LC@TSP (28.22% ± 4.81) had the slowest release behavior of P without a significant difference between the two. These results were explained by the high elasticity, high tensile strength, high elongation at break, hydrophobicity, and low water solubility of lignin-carrageenan/PEG composites. However, the addition of plasticizer to lignin-carrageenan formulations did not significantly modify the mechanical and surface properties of the composites. In conclusion, lignin-/PEG formulation composites with high swelling and water absorbency capacity and slow-release behavior could be more effective in agriculture and in the sustainable chemistry of phosphorus.

AUTHOR INFORMATION

Corresponding Author

*E-mail: abdellatif.barakat@inra.fr.

ORCID

Abdellatif Barakat: 0000-0003-4196-4351

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS USED

C, carrageenan; CA, contact angle; ε_b, elongation at break; E, tensile modulus; σ_s, tensile strength; FTIR, Fourier transform infrared spectroscopy; L, lignin; OP, olive pomace; PEG, polyethylene glycol 2000; RH, relative humidity; SEM, scanning electron microscopy; TGA, thermogravimetric analysis; TSP, triple superphosphate

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New generation of controlled release phosphorus fertilizers based on biological macromolecules: Effect of formulation properties on phosphorus release

Saloua Fertahi [a,b,c,e], Isabelle Bertrand [a], Mohamed Ilsouk [b], Abdallah Oukarroum [b], M'Barek Amjoud [c], Youssef Zeroual [d], Abdellatif Barakat [b,e,*]

[a] Eco&Sols, Univ Montpellier, CIRAD, INRA, IRD, Montpellier SupAgro, 2, Place Pierre Viala, 34060 Montpellier, France
[b] Mohammed VI Polytechnic University (UM6P), Hay Moulay Rachid, 43150 Ben Guerir, Morocco
[c] LMCN, Faculté des Sciences et Techniques Guéliz, Université Cadi Ayyad, 40000 Marrakech, Morocco
[d] OCP/Situation Innovation, OCP Group, Jorf Lasfar Industrial Complex, BP 118 El Jadida, Morocco
[e] IATE, Univ Montpellier, CIRAD, INRA, Montpellier SupAgro, 2, Place Pierre Viala, 34060 Montpellier, France

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ABSTRACT

The main objective of this work was to study the possibility of using polysaccharides and lignin as a coating material for water-soluble triple superphosphate (TSP) granular fertilizers. In this study, composites based on three polysaccharides (sodium alginate (alginic acid sodium salt): AL, kappa-carrageenan: CR and carboxymethyl cellulose sodium salt: CM) and lignin (LG) were prepared. The lignin used was extracted from olive pomace (OP) biomass using the alkali method. The morphological, mechanical, and surface properties as well as the thermal behavior of the coatings were characterized and compared. Their morphology and thickness revealed by scanning electron microscopy (SEM) showed good adhesion between the fertilizer and coating materials. The results showed that the lignin-carrageenan formulation (LGCR) exhibited the highest water absorbency and elastic modulus. Release tests showed the effect of the TSP/biopolymer mass ratio and that the slowest P release was obtained with the LGCR@TSP formulation composite within 3 day. In addition, 59.5% and 72.5% of P was released after 3 days with the TSP/biopolymer mass ratios of 5/1 and 15/1, respectively, compared to 100% P release with the uncoated TSP.

1. Introduction

Recently, much attention has been paid to fertilizers with slow release and water retention properties due to their essential roles in the development of sustainable agriculture and horticulture [1]. Plant growth and yield mainly rely on the nutrients available in soil and water. When soil nutrients are missing or in short supply, fertilizers, mostly of chemical origin, are applied. Their use is open to criticism because of their price, their negative impact on the environment (water and air pollution) and the fossil origin of phosphorus fertilizers. Phosphorus fertilizers are one of the most highly demanded because P is often the most limiting plant nutrient [3]. This is not because the amount of total P in soil is low but rather because the P in soils is in chemical forms that are not available to plants [2,3]. The world phosphate fertilizer demand is expected to reach 45.858.000 tons (P_2O_5) in 2020, while it was 41.151.000 tons in 2015 [4]. However, due to the low efficiency of soil P fertilizers, only 10–20% of this P is taken up by plants [1,5,6]. The currently available forms of P fertilizers require further improvements to increase their bioavailability in soils. Controlled-release fertilizers (CRFs) may improve the efficiency of P fertilizers while reducing their negative environmental effects [7,8]. CRFs employ either coating or encapsulation of mineral fertilizers in polymeric matrices. CRFs use is a new trend and a good alternative to conventional fertilizer to reduce fertilizer consumption and loss and to alleviate the negative environmental effects of chemical fertilizers. In most cases, the fertilizer granule is encapsulated inside an inert material [9]. The coating layer acts as a physical barrier that controls nutrient release [7]. The release behavior of water-soluble fertilizers depends on many parameters, including the porosity and structure of the coating material, coating thickness, granule size and form, soil temperature and pH, humidity and microbial activity [7,10–12]. The coating materials applied most frequently are sulfur [13,14], waxes [15], polystyrene [16], polyethylene [15,17,18], poly(N-isopropylacrylamide) [19,20], polyurethane [19], polysulfone

* Corresponding author at: IATE, Univ Montpellier, CIRAD, INRA, Montpellier SupAgro, 2, Place Pierre Viala, 34060 Montpellier, France.
E-mail address: abdellatif.barakat@inra.fr (A. Barakat).

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[21–24], polyacrylonitrile [23,24], etc. However, the combination of fertilizer and polymeric coatings has some disadvantages. The majority of synthetic polymers require organic solvents (e.g., *N*-dimethylformamide [24], chloroform [25]) for solubilization, which are harmful to the environment. In addition, the polymers remain in the soil when the nutrients are exhausted. According to Trenkel [26], the use of polymeric materials in coatings could lead to an undesirable accumulation of plastic residues of up to 50 kg/ha/year. The development of environmentally friendly CRFs using biodegradable polymers derived from biomass, agricultural and agro-industrial waste (carbohydrates, lignin, etc.) is a much better solution. Compared to synthetic polymers, biological macromolecules are relatively inexpensive [27]· biodegradable, nontoxic for soil organisms and contribute to the improvement of soil properties [28,29]. In addition, biological polymers appear to be a potential alternative to synthetic polymers for CRFs coatings [30] and could contribute significantly to organic waste recycling and the circular economy. Lignin is a cheap and natural polymer available as a waste material, as it is recovered mainly as a byproduct from wood pulping processes, with approximately 100 million tons produced annually worldwide [31]. Moreover, compared to other polymers, lignin is a renewable, biodegradable, amorphous, relatively hydrophobic biopolymer that is rich in recalcitrant carbon, which could contribute to increasing the soil organic matter content [9]. Studies using commercial lignin blended with additives as a coating agent (rosins and linseed oil [8,9], alkenyl succinic anhydride [32]) showed its efficiency at decreasing the release rate of nutrients from fertilizers. Polysaccharides are also used in coating formulations. However, these compounds have never been tested alone. They are always mixed with other polymers or other components, such as clays [33]. Wan et al. [34] reported that k-carrageenan-Na-alginate and k-carrageenan-g-poly(acrylic acid)/celite composite superabsorbents were used as inner and outer coating materials, respectively, for nitrogen fertilizer. This double-coated fertilizer had slow-release behavior and improved the water-holding capacity and water-retention properties of the soil.

This work is a continuation of the investigations of new biobased formulations for CRF production, initiated in our previous work recently published [30]. This study for objective to use extracted lignin from olive pomace (OP) biomass and some commercial polysaccharides (alginates (AL) from brown algae, carrageenan (CR) from red algae and carboxymethyl cellulose (CM) from wood pulp) for the preparation of different formulations composites for TSP fertilizer coating. The choice of these polysaccharides is based on the availability and dissimilarity of their basic materials (algae and wood), their ability to form films and their high water absorption capacity [34]. The main objective of this research was to evaluate the influence of different biopolymers coatings on the P release behavior of CRF granules.

2. Experimental section

In this study, OP was used for lignin extraction. OP was provided from a Moroccan olive press (*Tadla* region). Kappa carrageenan (CR) (CAS: 1114-20-8), sodium alginate (AL) (CAS: 9005-38-3), sodium carboxymethyl cellulose Mw~700.000 (CM) (CAS: 9004-32-4), potassium carbonate K_2CO_3 (CAS: 584-08-7), sodium hydroxide NaOH (CAS: 1310-73-2) and phosphorus pentoxide (P_2O_5) (CAS: 1314-56-3) were purchased from Sigma-Aldrich. Triple superphosphate (TSP), a granular phosphate fertilizer (46% P_2O_5), was produced and offered by OCP group, Morocco.

2.1. Lignin polymer extraction from OP biomass

The lignin polymer used in this study was extracted from OP biomass using the alkali method. Details of the lignin (LG) alkali extraction and the chemical and structural analysis of the OP and LG were presented and discussed in our previous work [30]. The elementary composition of the LG biomass was estimated to be 58.24 ± 0.01% C, 7.89 ± 0.03% H, and 28.05 ± 0.07% O, and the C/N ratio was 32.54.

2.2. Preparation of formulations and polymer-based films

Formulations and composite films were prepared using lignin solution (LG), alginate (AL), carboxymethyl cellulose (CM), and carrageenan (CR) in different ratios (Table 1). Black liquor (33.34 g/L) was used directly without stirring for lignin formulation and film preparation. Polysaccharide solutions (AL, CM, CR) were prepared separately in water (0.5 *w*/w%) under constant stirring for 2 h at ambient temperature (Table 1). The lignin-polysaccharide-based composites were prepared as follows: 80% lignin was mixed with 20% polysaccharides (w/w). All solutions were stirred overnight at room temperature. The same formulations were used for composite film preparation and TSP fertilizer coating. For the film preparation, the mixtures were deposited onto square Petri dishes (12 cm), and the water was evaporated by drying overnight at 40 °C. Films were made in triplicate.

2.3. Characterization of lignin-polysaccharide composite films

2.3.1. Contact angle

The hydrophobicity of the composite films was evaluated by analyzing the behavior of water drops injected onto their surfaces. Before contact angle measurements, films were cut into small rectangles (0.5 cm * 2 cm), and their support sides were glued to glass slides using double-sided tape. Samples were equilibrated for 5 days at 46% relative humidity (RH) in a desiccator in the presence of K_2CO_3-saturated solution. A humidity detector was used to verify the obtained humidity. Contact angle measurements were realized with a goniometer (Digidrop, GBX, France) equipped with a diffuse light source and a CCD camera (25 frames/s). A droplet of ultrapure water (~3 μL) was deposited on the film surface with a precision syringe (Teflon needle, 0.82 mm external diameter). The method is based on image processing and curve fitting for the contact angle. The video was analyzed frame-by-frame with GBX software to determine the contact angle as a function of time [35,36]. Three measurements were performed on each sample.

2.3.2. Mechanical properties

The film elasticity (tensile modulus EM), tensile strength (TS) and elongation at break (EB) were studied using tensile tests. Tests were performed on films using a texture analyzer (TA. XT plus). The tensile specimens were cut into rectangles (80 mm in length and 10 mm in width). The gauge length was fixed at 30 mm, and the speed of the moving clamp was 5 mm/min [37]. Measurements were carried out at room temperature. Three replicates were characterized, and the results are reported as average values with standard deviations.

Table 1
Composition of prepared formulations. LG: lignin, AL: alginate, CM: carboxymethyl cellulose, CR: carrageenan, LGAL: lignin-alginate, LGCM: lignin- carboxymethyl cellulose, LGCR: lignin-carrageenan.

Polymers-based formulations	LG (%)	AL (%)	CM (%)	CR (%)
LG	100	0	0	0
AL	0	100	0	0
CM	0	0	100	0
CR	0	0	0	100
LGAL	80	20	0	0
LGCM	80	0	20	0
LGCR	80	0	0	20

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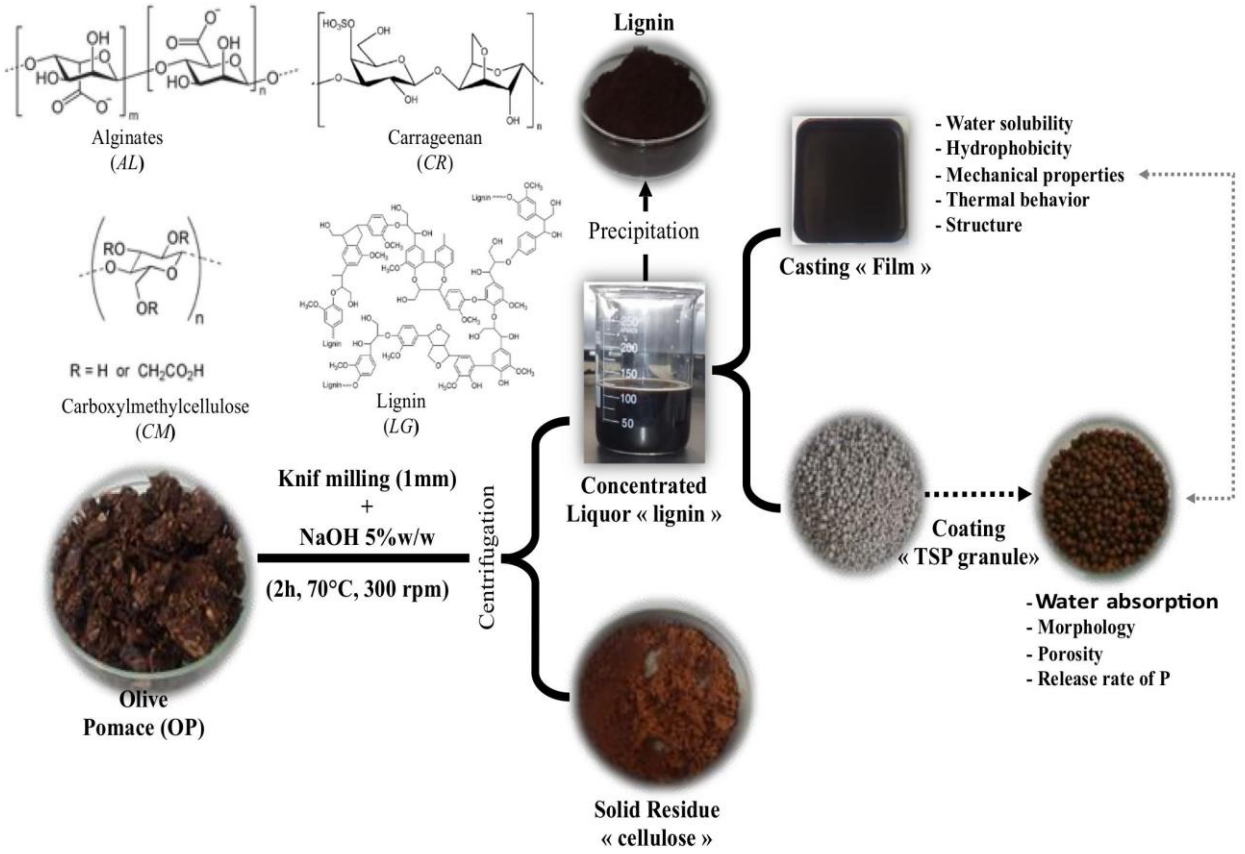

Scheme 1. Extraction details of lignin from OP and strategies used to coat TSP fertilizer and to characterize the coating agents

2.3.3. Thermogravimetric analysis (TGA)

The different formulations were analyzed using TGA. TGA was conducted under nitrogen (with a flow rate of 50 mL/min) using a TGA instrument (Mettler Toledo) with a 5 °C/min heating rate from 25 to 900 °C. Ash content was determined under air (with a flow rate of 50 mL/min) with an isothermal segment (900 °C for 1 h).

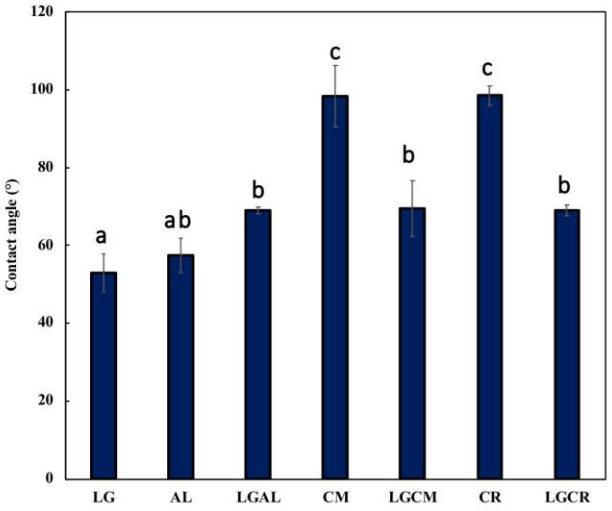

Fig. 1. Contact angle of composite films, LG: lignin, AL: alginate, CM: carboxymethyl cellulose, CR: carrageenan, LGAL: lignin-alginate, LGCM: lignin-carboxymethyl cellulose, LGCR: lignin-carrageenan. Different letters between treatments indicate significant differences ($P < .05$, $n = 3$).

2.4. Preparation and characterization of TSP fertilizer coatings

Granules of TSP fertilizer were sieved to select homogeneous granules with diameters of 2–3 mm and then placed into a rotary drum (12 rpm, capacity of 11 L) developed in our laboratory. The distance between the spray nozzle and the center of the rotary drum was 25 cm. Fifty grams of TSP granules were covered with a layer of different formulations (3.33 g) based on lignin and polysaccharides by spraying at regular time intervals. The mass ratio of TSP/polymer was 15/1. Then, the coated TSP granules were continuously dried in the rotary drum by a hot air stream (65 °C). To study the effect of the solution concentration on coating thickness and phosphorus release behavior, the mass concentration of the coating solutions was tripled (the ratio of TSP/polymer was 5/1).

2.4.1. Morphology and thickness of the coating layer

The morphology of the coated TSP was evaluated by a tabletop scanning electron microscopy (SEM) (Phenom ProX, Phenom-World) using a backscattered electron detector (acceleration voltage of 10 kV, mode image). Three granules of each type of coated TSP fertilizer were randomly chosen. These granules were cut in half with a razor blade and fixed on a support using double-sided tape. To measure the thickness of the coating layers, the drawing rule option of the SEM was used, and three measurements were performed on different areas of each granule.

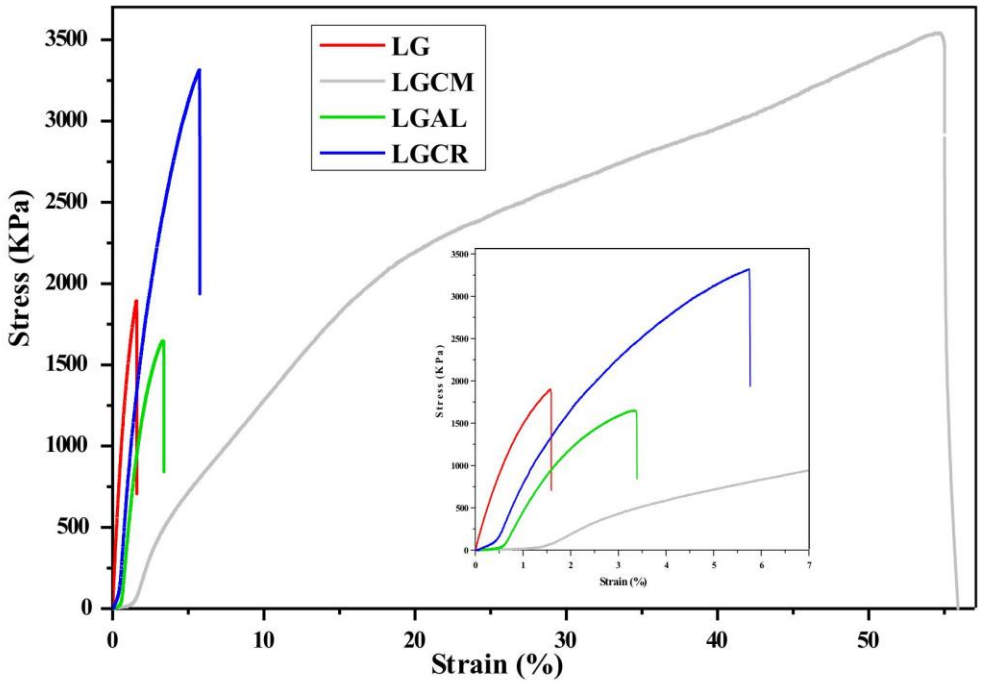

Fig. 2. Typical stress-strain curves of film composites: LG: lignin, AL: alginate, CM: carboxymethyl cellulose, CR: carrageenan, LGAL: lignin-alginate, LGCM: lignin- carboxymethyl cellulose, LGCR: lignin-carrageenan, n = 3.

2.4.2. Hygroscopicity of uncoated and coated TSP

Coated TSP granules were dried at 50 °C in a vacuum oven in the presence of P_2O_5. Samples were weighed to a constant weight (complete drying). Then, they were conditioned in humidity-controlled rooms at three relative humidities: 35, 60 and 80%. The water absorbency of the coated TSP was monitored for 3 days [8]. Samples were weighed every 24 h, and the water absorption was determined by the weight difference between dried and conditioned samples. All the determinations reported here are triplicate results with standard deviations.

2.5. Slow release behavior of coated TSP in water

For release experiments, uncoated and coated fertilizers were equilibrated for 3 days at 60% RH. Then, 0.25 g of each type of coated TSP was immersed in 50 ml of distilled water in glass bottles. The bottles were conditioned at a constant temperature of 25 °C. After 1 and 6 h, and 1, 2, 3, 4 and 5 days, 1 ml of the different solutions was sampled for phosphorus concentration determination, and an additional 1 ml of distilled water was added to the bottles to maintain a constant volume. All release experiments were carried out in triplicate. The phosphorus concentration was determined using the colorimetric molybdenum vanadate method [24]. The phosphorus release at each time was obtained by Eq. (1), which was proposed by Rashidzadeh et al. [38] and expressed in relation to the phosphorus concentration and total weight of phosphorus contained in the TSP fertilizer. All the determinations reported here are triplicate results.

$$\mathrm{CR}\ (\%w/w) = \frac{V_e \sum Cp_i + V_0\, Cp_n}{mp_0} * 100 \quad (1)$$

where CR is the cumulative amount of phosphorus released (%) from the TSP fertilizer, *Ve* is the sampling volume, V_0 is the initial volume of the release media, Cp_i and Cp_n are the phosphorus concentrations (mg/ml), *i* and *n* are the sampling times, and mp_0 is the total weight of phosphorus contained in the TSP fertilizer.

Table 2
Tensile modulus (EM), tensile strength (TS) and elongation at break (EB) of composite films. LG: lignin, LGAL: lignin-alginate, LGCM: lignin-carboxymethyl cellulose, LGCR: Lignin-carrageenan, $n = 3$.

Formulation	EM (KPa)	TS (KPa)	EB (%)
LG	786,93 ± 385^{ab}	1135.09 ± 766^{a}	1.46 ± 0.11^{a}
LGCR	1191,51 ± 356^{a}	3674.11 ± 318^{b}	9.37 ± 1.99^{b}
LGCM	225.49 ± 96^{b}	2510.98 ± 754^{ab}	43.94 ± 15.99^{c}
LGAL	612.53 ± 65^{ab}	1653.57 ± 261^{a}	2.79 ± 0.43^{a}

Within a column, means followed by the same letter are not significantly different.

2.6. Data analyses

The average values were calculated for each treatment. Analysis of variance (ANOVA), mixed models and correlation matrixes among treatments were performed using R version 3.4.2. The effect of formulation on contact angle (CA), Young's modulus (EM), tensile strength (TS), elongation at break (EB), and thickness of the coating agent was tested by one-way ANOVA. Mixed models ((Package: lme4) were performed to analyze the effect of formulation and time and on P release with formulation and time as fixed effects and the bottle (containing fertilizer and water) as a random effect. If significant, Tukey's (for ANOVA) and Emmeans (for mixed models) post hoc tests were used for pairwise multiple comparisons ($p < .05$). Correlations between films and coated TSP characteristics (treated with lignin and lignin-polysaccharides) were analyzed using a correlation matrix.

3. Results and discussion

Different lignin-polysaccharide formulations were prepared using alkali extracted lignin from OP residue (Scheme 1). The objective of this study was to develop a new generation of coating formulations

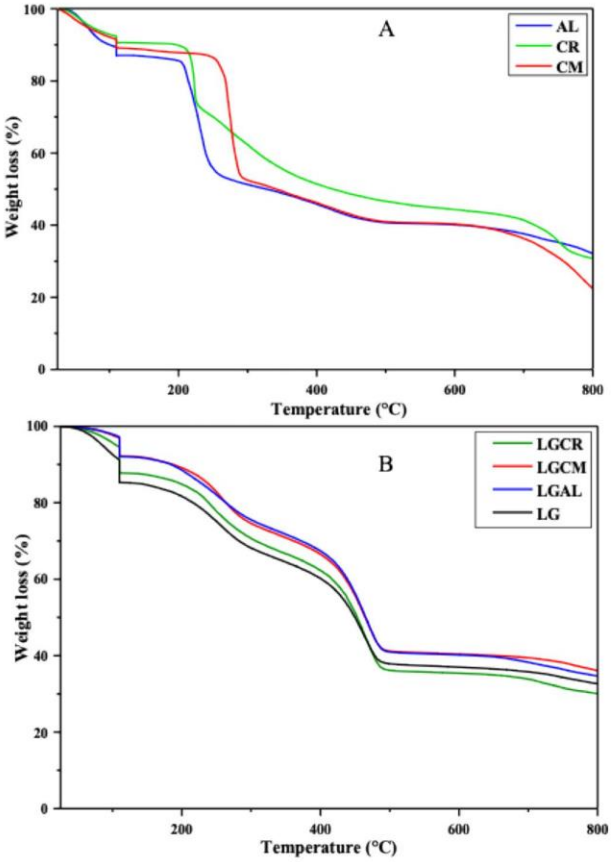

Fig. 3. TGA of (A) polysaccharide films (AL: alginate, CM: carboxymethyl cellulose, CR: carrageenan) and (B) LG and composite films (LG: lignin, LGAL: lignin-alginate, LGCM: lignin- carboxymethyl cellulose, LGCR: lignin-carrageenan).

based on lignin and polysaccharides and to study the effect of the biopolymers type on the formulation properties. Finally, this study sought to correlate the physicochemical properties of different composite formulations on the P release behavior. For this purpose, we utilized two strategies (Scheme 1):

i) Preparation of composite films and study of their surface, mechanical and thermal properties.
ii) Coating of TSP granules using the same formulations and study of their water absorption, morphology and P release.

3.1. Lignin-polysaccharide composite formulations

3.1.1. Surface properties (contact angle)

The hydrophobic surface corresponds to a contact angle >60°, while a contact angle <60° corresponds to a hydrophilic surface [36]. A significant difference in contact angle was observed between different formulations (p-value <.05) (Fig. 1). The hydrophobicity of formulation composites decreased in the following order: CM = CR > > LGCM = LGAL = LGCR> AL = LG. No significant difference was observed between CM (98°) and CR (98°) films, which are more hydrophobic than alginate and lignin film composites with contact angles of 57° and 53°, respectively. The low contact angle of the lignin film could be attributed to the presence of $HO^{-}Na^{+}$ groups in lignin (after solubilization in NaOH) (Schema 1).

Notley and al [39] reported that the contact angles of softwood kraft lignin and softwood milled wood film (thickness: 50–60 nm) were 46, 52.5 and 55.5°, respectively. Norgren [40] also reported that softwood lignin films with a thickness of 20–140 nm had a contact angle of 46°, which is in good agreement with our study. In another study, Ramirez et al. [41] reported that the contact angle of CM was estimated to be 83, compared to 98° obtained for CM in this study. This difference could be due to the difference in the total solid content, the thickness of the CM composite film and the surface roughness. Lijun Yang et al. [42] obtained for alginate film a contact angle of approximately 59° compared to 53° obtained in this study. They attributed this value to the hydrophilic surface of this material due to hydrophilic hydroxyl functional groups in the AL polymer (Scheme 1). The contact angle obtained for CR was 98° in agreement with Karbowiak et al. [36] The contact angle of iota-carrageenan ranged between 88.3°–115.2°. The authors attributed this hydrophobic behavior of the iota-CR film to the three-dimensional helical structure of the carrageenan polymer, with strong intramolecular hydrogen bonding beneath the film surface and no orientation of polar groups at the surface. Jayasekara et al. [43] also observed this phenomenon with starch composite film. We also observed that the addition of lignin (LG) to the polysaccharide formulation with a mass ratio of 4/1 (LG/polysaccharides) modified the hydrophobicity of the composite formulations (Fig. 1). The presence of lignin in the formulation tends to decrease the surface hydrophobicity of lignin-polysaccharide composites. Shankar et al. [44] observed the same phenomenon. They reported that the contact angle of agar-lignin films was lower than that of agar films, and this reduction in contact angle might be due to the roughness of the film after the addition of lignin.

3.1.2. Mechanical properties of composite films

Fig. 2 shows the typical stress-strain curves of different composite films. The elastic modulus (EM), tensile strength (TS) and elongation at break (EB) depends on the type and structure of the polysaccharides in the composites (p-value <.05) (Table 2). The EM, TS and EB of the obtained composite films varied between 225 and 1191 KPa, 1135–3674 KPa and 1.5–44%, respectively. The TS of the lignin (LG) film was 1135.09 ± 766 KPa, which is lower than that of the polysaccharide-incorporated composite films (Table 2). Aadil et al. [36] reported that the tensile strength of lignin films extracted from acacia wood and blended with alginate was 413 ± 2 KPa, while the tensile strength increased to 625 ± 7, 569 ± 12, 466 ± 6 KPa with the addition of the different plasticizers, glycerol, epichlorohydrin and PEG 4000, respectively. Lignin extracted from OP (this study) has a greater tensile strength than acacia wood lignin, even when blended with alginate and plasticizers. This is probably due to the presence of fatty acids in lignin from OP, as discussed in our previous work [30]. Fatty acids are usually used as plasticizers in composite formulations [45], and their presence can play a role in natural plasticizers in different lignin formulations. The lignin-carrageenan (LGCR) composite exhibited higher EM (1191 KPa) and TS (3674 KPa) than the LGAL and LGCM composite films. We can also see from the results that TS and EB were significantly increased by 224% and 542%, respectively, with the addition of CR compared to LG, while the addition of CM significantly increased the EB by 2910%. This increase in EB compared to LG film can be explained by the hygroscopicity of polysaccharides. These compounds are more hygroscopic than LG polymers; hence, water uptake could explain the plasticization behavior [46]. However, in the case of lignin loaded with alginate, no strong effect on mechanical properties was observed compared to the LG film. The lignin polymer has a tridimensional and porous surface structure that might aid in compatibility with the polysaccharides [49]. These phenomena have also been observed in the plant cell wall, confirming the lignin-polysaccharide interaction [48,49].

3.1.3. Thermogravimetric analysis (TGA)

The thermal stability and degradation behavior of polysaccharides and lignin-polysaccharide composites were assessed using TGA and weight loss curves. Fig. 3A presents the TGA analysis of

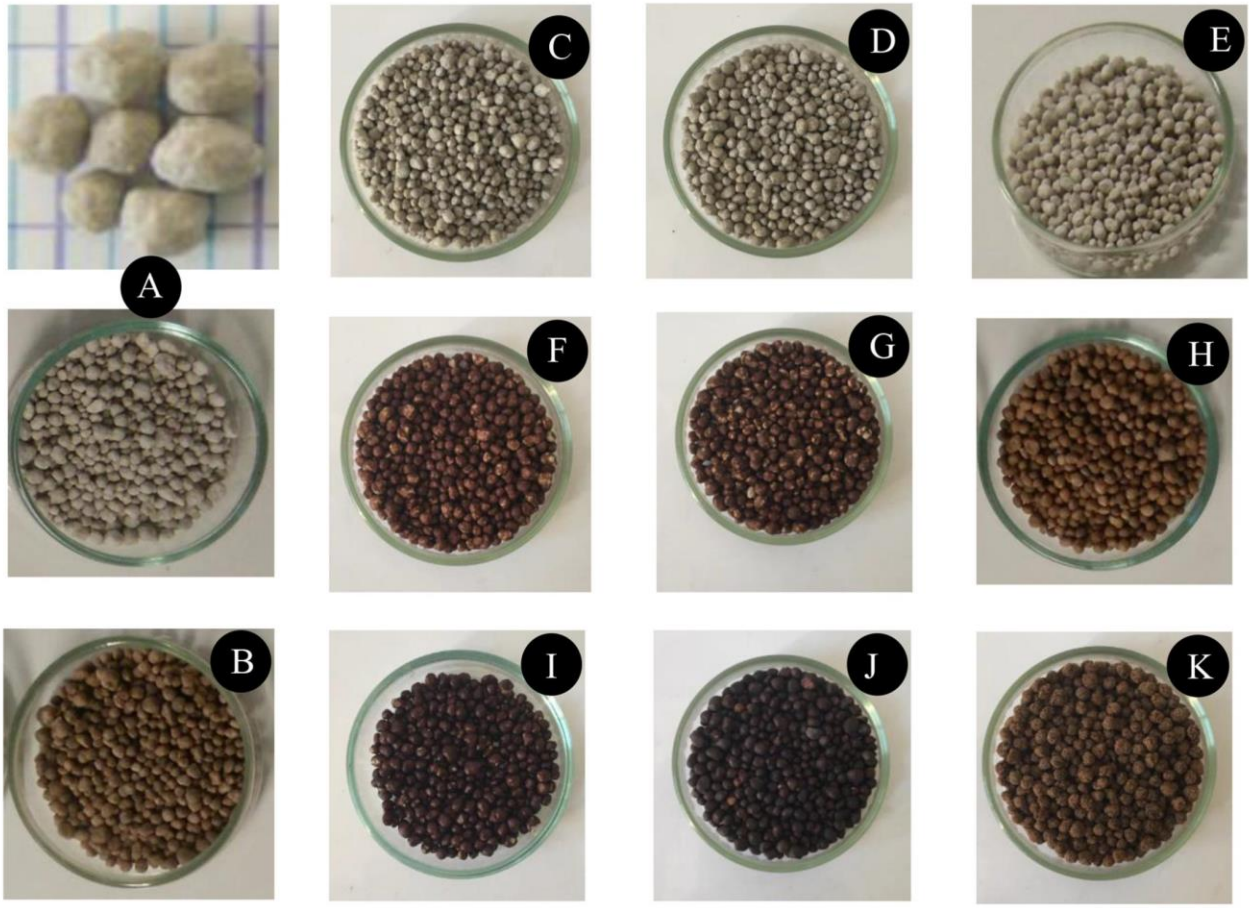

Fig. 4. Real image of noncoated TSP (A) and coated TSP at the TSP/polymer ratio of 15/1 with (B) LG (lignin), (C) AL (alginate), (D):CM (carboxylmethyl cellulose), (E) CR (carrageenan), (F) LGAL, (G) LGCM and (H) LGCR, and at the TSP/polymer ratio of 5/1 with (I) LGAL, (J) LGC and (K) LGCR.

the polysaccharide films. From these curves, we can observe that the thermal degradation of all polysaccharides occurs in three steps. The first step at 25–105 °C corresponds to water desorption, with approximately 9–13% overall weight loss due to dehydration. The second decomposition stage starts at 192 °C for the AL and CR films and 230 °C for the CM film. This step is attributed to the thermal degradation of polysaccharides. In the last step, the AL and CM films lost approximately 50% of their weight at 340 °C, while the CR film had to reach 422 °C to lose the same percentage of weight. This mass loss is related to the formation of byproducts of polysaccharides during the thermal degradation process [50]. Based on the TGA analysis (Fig. 3B) of LG and composite films, the lignin film had fast thermal degradation compared to the lignin-polysaccharide blended film. The thermal behavior of the LGAL and LGCM composites seemed to be similar. These films exhibited the slowest thermal degradation, followed by the LGCR and LG films. The 50% weights of LG and LGCR were lost at 450 °C and 454 °C, respectively, while LGCM and LGAL lost 50% of their initial mass at 464 °C.

The blending of lignin with polysaccharides enhanced the thermal stability of the three materials. LG, CM and CR films underwent the active weight loss step at 25–290 °C, while this step occurred at 25–500 °C with the addition of lignin. In general, the mass loss of composite-polymer films occurred between 25 and 500 °C [51,52]. Changhua Liu [51] reported similar intervals of degradation temperatures of lignin-poly (4-vinylpyridine) films.

3.2. Coated TSP fertilizer properties

3.2.1. Morphological characterization of coated TSP fertilizers

Fig. 4 presents pictures of coated TSP. The interactions of TSP granules and coatings were observed using SEM (Fig. 5). The thickness of the coating layers was determined for the coated TSP fertilizers. The thickness of the layers (TSP/polymer ratio of 15/1) was 71.3 ± 23.6 μm on average. The coating formulation has no significant effect on coating thickness (p-value >.05).

The coating thickness is an important parameter that can control the nutrient release rate [24,53]. The effect of two ratios of TSP/polymers (15/1 and 5/1) on the coating agent thickness was studied, and the results are shown in Fig. 6. A significant effect on coating agent thickness was observed between ratios for the granules coated with the three formulations. The coatings formed with a higher polymer concentration exhibited higher thickness (135.6 ± 20.9 μm) for the TSP/polymer ratio of 5/1 than the 71.3 ± 23.6 μm observed for the TSP/polymer ratio of 15/1. This result is in agreement with the previous report of Anna Jarosiewicz et al. [24], suggesting an increase in the thickness with increasing polymer concentration in the coating solution.

3.2.2. Hygroscopicity of uncoated and coated fertilizers

Fig. 7 illustrates the water absorption of uncoated and coated TSP within 3 days at different RHs (35%, 60% and 80%). The water absorption of all formulations increased with increasing air humidity and with time. LGCR@TSP, LGAL@TSP and LGCM@TSP exhibited the highest

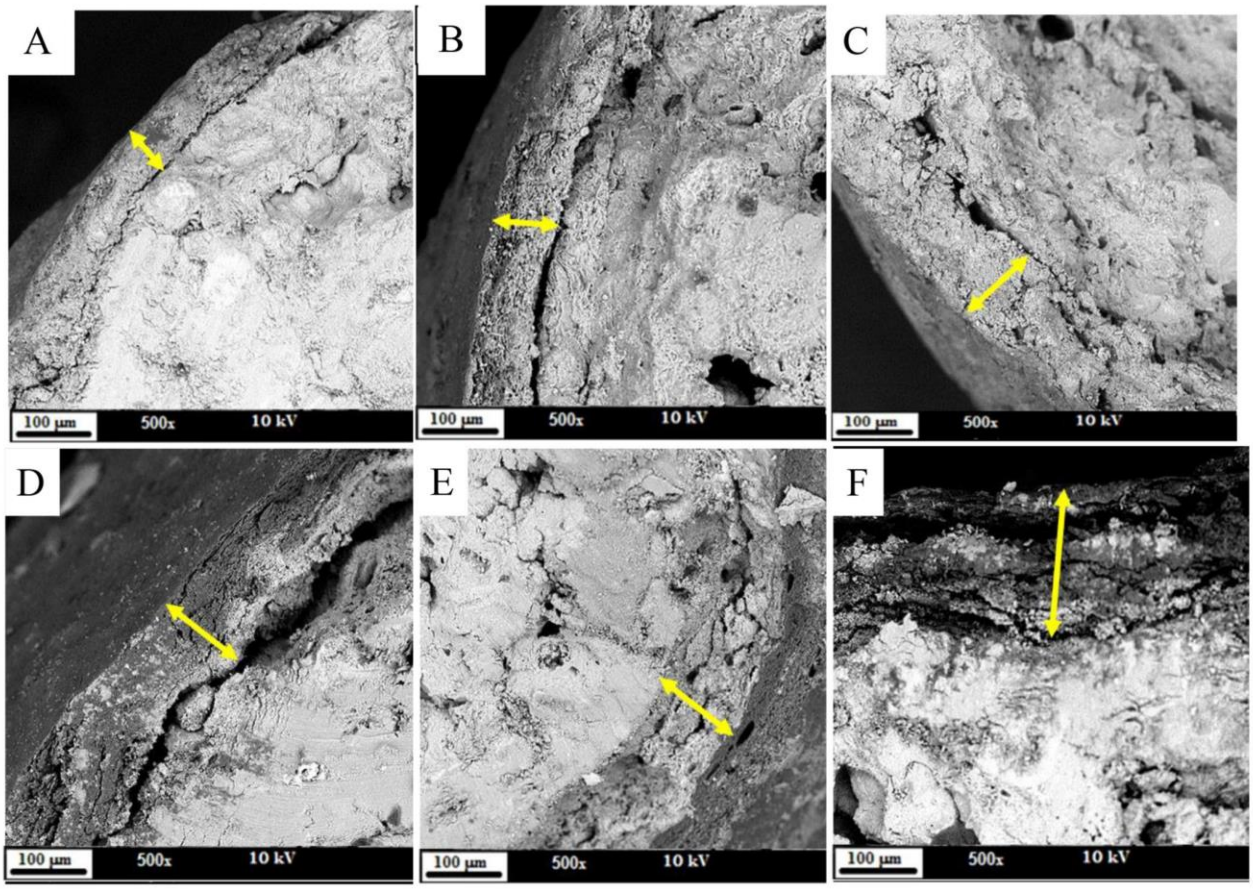

Fig. 5. SEM of cross-section of the coated TSP fertilizer at the TSP/polymer mass ratio of 15/1 with (A) LGAL (lignin-alginate, (B) LGCM (lignin- carboxymethyl cellulose and (C) LGCR (lignin-carrageenan) and at the TSP/polymer ratio of 5/1 with (D) LGAL, (E) LGCM and (F) LGCR.

hygroscopicity in the following order: LGCR@TSP > LGAL@TSP > LGCM@TSP. According to Liang et al. [54], the water absorption of coating polymers depends on many factors, such as the amount of hydrophilic groups and elasticity of the polymer networks. As previously mentioned in Table 2, LGCR exhibited the highest elastic modulus (EM) (1191.51 ± 356 KPa), followed by LGAL (612.53 ± 65 KPa) and then LGCM (225.49 ± 96 KPa). The major result was that the water absorption of the coating increased when the elasticity increased, which could improve the swelling properties of the coated fertilizers. It is noteworthy that a coated fertilizer with swelling and slow release behavior could effectively improve the utilization of both fertilizer and water resources [54].

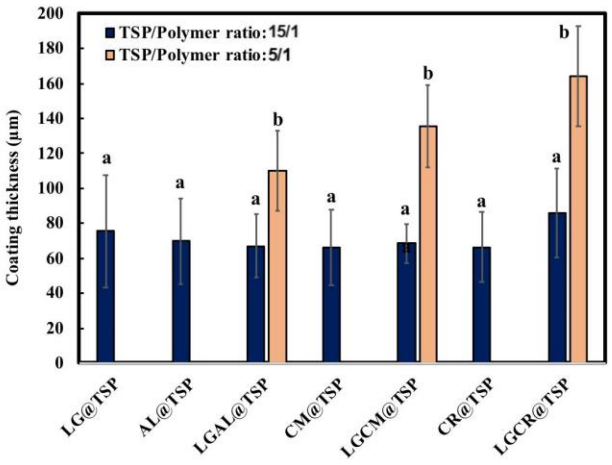

Fig. 6. Thickness of coating layers on TSP granules coated with LG (lignin), AL (alginate, LGAL (lignin-alginate), CM (carboxylmethyl cellulose), LGCM (lignin-carboxylmethyl cellulose), CR (carrageenan) and LGCR (lignin-carrageenan). Different letters between treatments indicate significant differences ($P < .05$, $n = 9$).

3.3. Slow-release behavior of phosphorus from coated TSP fertilizers

As shown in Table 3, the untreated TSP released approximately 72 ± 0.4, 85 ± 140 and 99.5 ± 4.3% of P within 6, 24, and 72 h, respectively. In contrast, the fertilizers coated with only lignin or only polysaccharides or with lignin-polysaccharides (the TSP/polymer ratio of 15/1) released only 19.3–55.7%, 52–77.1% or 68.3–80.6% within 6, 24, and 72 h, respectively. Statistical analysis showed a significant effect of coating formulation and time on the delay of P release ($p < .05$). The slowest P release was observed with the LGCR@TSP formulation within the first and second days.

To understand the relationship between P release behavior and the physicochemical properties of film composites of coated TSP discussed previously in this work, a correlation matrix was constructed (Fig. 8). P release is strongly negatively correlated with EM ($R = -0.81$), while it is strongly positively correlated with EB ($R = 0.93$). The young modulus (EM) represents the elastic deformation. When the

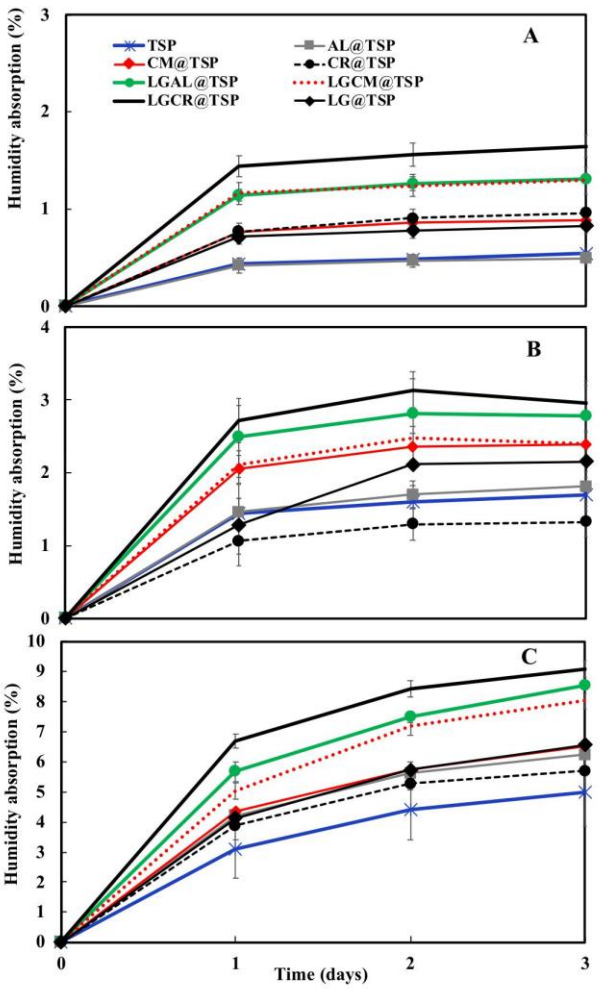

Fig. 7. Water absorption (WA) of uncoated and coated fertilizers over time at different relative humidities: (A) 35%, (B) 60% and (C) 80% RH with LG (lignin), AL (alginate), CM (carboxylmethyl cellulose, CR (carrageenan) LGAL (lignin-alginate), (G) LGCM (lignin-carboxylmethyl cellulose) and LGCR (lignin-carrageenan), $n = 3$.

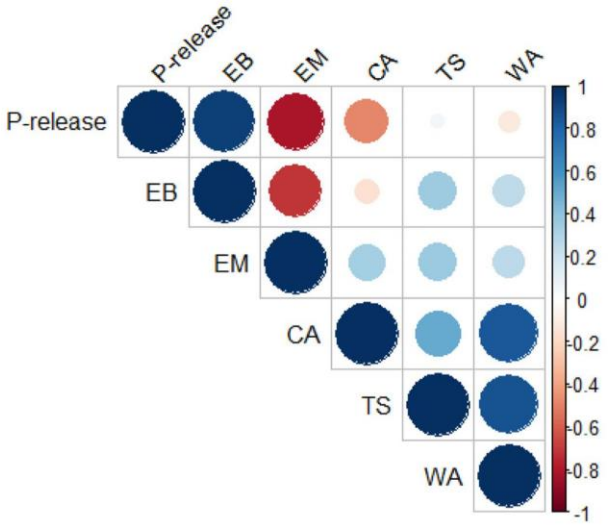

Fig. 8. Correlation matrix between the properties of composite films and coated TSP. Film properties: EM (elastic modulus), TS (tensile strength), EB (elongation at break) and CA (contact angle). Coated TSP properties: P release within 1 day and WA (water absorption at RH 35% within 1 day). Positive correlations are displayed in blue, and negative correlations are displayed in red. Color intensity and circle size are proportional to the correlation coefficient, R. On the right side of the correlogram, the legend color shows the correlation coefficients and the corresponding colors. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

coating material is elastic, the shell is able to resist the internal pressure created inside the core upon contact with water, and the P is released slowly without the shell being destroyed. A moderate negative correlation between P release and CA was also revealed ($R = -0.49$). This phenomenon could be explained by the fact that, when the contact angle is large, the coating material is hydrophobic, and then the affinity between the layer and water is weak. This lack of affinity prevents the penetration of large quantities of water inside the fertilizer core and then decreases the dissolution of TSP. For TS and WA, a weak or no correlation was observed with P release ($R < 0.11$). From these data and discussion, we concluded that the LGCR formulation is the most efficient coating for mineral fertilizer due to its high elastic modulus, high CA, high water absorption and, as a consequence, slow release of P.

The release behaviors of TSP coated with LGCR, LGCM and LGAL formulations at TSP/biopolymer ratios of 15/1 and 5/1 are shown in Table 3. A statistical study showed a significant effect of TSP/biopolymer ratios (the effect of coating thickness) on the release response from LGAL@TSP and LGCM@TSP (p-value < .05) but not LGCR@TSP. As previously presented in Fig. 5B, a high TSP/biopolymer ratio resulted in a high thickness. A higher polymer coating concentration decreased the P release of coated TSP granules due to the increase in coating layer thickness. After 3 days, TSP coated with LGCR, LGCM and LGAL formulations at the TSP/biopolymer ratio of 15/1 (thickness = 71.3 ±

Table 3
Release behavior of TSP and coated TSP with different polymers in water, TSP coated with LG: lignin, AL: alginate, CM: carboxymethyl cellulose, CR: carrageenan, LGAL: lignin-alginate, LGCM: lignin- carboxymethyl cellulose, LGCR: lignin-carrageenan, n = 3.

Formulation	TSP/Polymer ratio	P-release in water (%) over time (h)					
		6	24	48	72	96	120
TSP	–	72.0 ± 0.4^{a}	85.0 ± 14^{a}	95.0 ± 2.7^{a}	99.5 ± 4.3^{a}	–	–
LG@TSP	15/1	34.3 ± 4^{ab}	55.5 ± 6.4^{a}	64.1 ± 1^{bc}	65 ± 9.8^{bcd}	71.6 ± 1.8^{abcd}	76 ± 0.7^{a}
CR@TSP	15/1	44.9 ± 4.9^{ab}	60.9 ± 0.7^{a}	69.5 ± 7.8^{ab}	78.1 ± 5.7^{abcd}	84.7 ± 15^{a}	90.2 ± 3.8^{b}
CM@TSP	15/1	39.7 ± 7.6^{ab}	77.1 ± 0.1^{a}	73.8 ± 4.7^{bc}	79.5 ± 3.5^{abc}	75.1 ± 1.7^{abc}	73.7 ± 1.1^{a}
AL@TSP	15/1	19.3 ± 13^{b}	76.7 ± 0.1^{a}	77.9 ± 6.6^{abc}	80.6 ± 10^{ac}	77.3 ± 5.5^{ac}	75.3 ± 4.4^{a}
LGCR@TSP	15/1	28.2 ± 4.8^{ab}	52.0 ± 6.5^{a}	59.0 ± 8.9^{abc}	72.5 ± 1.2^{abcd}	78.8 ± 2.0^{abcd}	75.3 ± 4.0^{abcd}
LGCM@TSP	15/1	55.7 ± 9.4^{ab}	66.7 ± 0.8^{a}	73.1 ± 4.8^{bc}	71.9 ± 0.5^{bcd}	69.6 ± 0.9^{abcd}	68.5 ± 1.1^{ad}
LGAL@TSP	15/1	51.7 ± 9.9^{ab}	74.5 ± 0.1^{a}	67.1 ± 1.7^{bc}	68.3 ± 3.1^{bcd}	68.7 ± 3.1^{abcd}	64.9 ± 0.5^{acd}
LGCR@TSP	5/1	–	59.1 ± 1.9^{a}	60.0 ± 1.0^{c}	59.5 ± 1.9^{bd}	60.4 ± 3.0^{bcd}	59.3 ± 1.6^{cd}
LGCM@TSP	5/1	–	59.9 ± 1.8^{a}	59.0 ± 1.4^{c}	58.9 ± 2.4^{d}	57.4 ± 0.8^{bd}	59.2 ± 2.2^{cd}
LGAL@TSP	5/1	–	56.3 ± 3.3^{a}	61.7 ± 3.9^{bc}	57.9 ± 5.5^{d}	55.1 ± 3.7^{d}	55.8 ± 3.5^{c}

Within a column, means followed by the same letter are not significantly different.

Annexes

Table 4
Comparative studies of different works using lignin as a coating material to control nutrient release.

Coating materials	Fertilizer	Granule size (mm)	T drying (°C)	Coating methods	Thickness (μm)	Release rate(%)		Ref
Lignin + Polysaccharides	TSP	2–3	65	Rotating pan	77–211	Noncoated Coated	100% after 3 d 57–58% after 3d	This work
Commercial lignin + rosins	TSP	2		Rotating pan	83–106	Noncoated Coated	80% after 3 days 20% after 3 days	Garcıa et al. [8]
Commercial lignins + plasticizers + hydrophobic compounds	Urea	–	70	Rotating pan	–	Noncoated Coated	>80% after 30 min 60–80%after 30 min	Mulder et al. [32]
Commercial lignin	Urea	0.5–5	–	Matrix	–	Non-treated Matrix	100% after <5 h 40–90% after 1 h	Perez et al. [57]

23.6 μm) released 72.5%, 71.9% and 68.3% of P, respectively, while TSP coated with the same formulations using a TSP/biopolymer ratio of 5/1 (thickness = 135.6 ± 20.9 μm) released only 59.5, 58.9 and 57.9% of P. These results are in accordance with other studies in the literature. Lubkowski et al. [55] showed that the release of phosphate from uncoated fertilizer was very fast and that all phosphates were released within 50 min, while coated NPK with different thicknesses (0.047–0.5425 mm) revealed a smaller release of phosphate in comparison with the initial NPK. Jarosiewicz et al. [24] showed that the release rate of NPK can be controlled by adjusting the thickness of the coating. They argued that NPK granules with double or triple-layered coatings (high thickness) released nutrients much slower than granules coated with one layer. NPK granules coated with one layer of 17% polyacrylonitrile (thickness ≈ 0.2 mm) released 93.7% of K^+ within 5 h, while granules with three layers of the same formulation (thickness ≈ 0.49 mm) released only 11.7%. Behin et al. [56] confirmed that the release of nitrogen depends strongly on the thickness of the coating. They reported that the dissolution rate decreases with increasing coating percentage. For urea coated with acetylated kraft lignin and sulfite lignin, dissolution rates of 88 and 97%, respectively, were obtained after 24 h for the sample with a 5.0% coating, whereas only 43 and 72% were obtained for the sample with a 15.0% coating.

Table 4 provides a comparative study of the results obtained in this work and those from previous studies using lignin as a coating material. It can be deduced from the work of Perez et al. [57] that using lignin alone does not improve the delayed release of urea in water, which can be explained by the presence of the polar groups on its surface and the resulting good affinity with water. Mulder et al. [32] also employed lignin coupled with plasticizers and some other hydrophobic compounds and reported that complete nitrogen release through these coating materials still occurred within 1 h. To improve its coating properties, lignin has also been mixed with rosins as a coating system for soluble fertilizers such as phosphate fertilizer [8] According to Garcia et al. [8], only 20% of P was released was this method. In comparison with these previous works, it can be concluded that our study is interesting in that we used low-cost materials based on OP, which can potentially be a good candidate for coating fertilizers and slowing the release rate of nutrients; however, our materials remain less efficient in this regard than synthetic polymers.

4. Conclusion

This work reports the valorization of lignin extracted from OP biomass with polysaccharides as a new coating material for water soluble TSP fertilizer. Films containing lignin and carrageenan show the best mechanical properties. The blending of lignin with polysaccharides reduced the hydrophobicity of the composites compared to that of the pure polysaccharide films but still showed higher hydrophobicity than the lignin film. The coating materials based on lignin and polysaccharides appear to have a good interaction and adhesion with the mineral fertilizer surface, confirming the effect of different formulations on the delay of P release. The results showed that >95% of P was released from uncoated TSP within 48 h, and 100% of P was released within 72 h, while the release of P with the lignin-polysaccahrides@TSP formulations decreased to approximately 60% within 72 h with a TSP/polymer ratio of 5/1.

CRediT authorship contribution statement

Saloua Fertahi: Investigation, Formal analysis, Writing - original draft, Writing - review & editing.**Isabelle Bertrand:**Supervision, Visualization, Writing - original draft.**Mohamed Ilsouk:**Investigation, Writing - original draft.**Abdallah Oukarroum:**Resources, Writing - original draft.**M'Barek Amjoud:**Supervision, Visualization.**Youssef Zeroual:** Funding acquisition, Visualization.**Abdellatif Barakat:**Project administration, Supervision, Writing - original draft, Writing - review & editing.

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Impact of Plasticizers on Lignin−Carrageenan Formulation Properties and on Phosphorus Release from a Coated Triple Superphosphate Fertilizer

Saloua Fertahi, Isabelle Bertrand, Mohamed Ilsouk, Abdallah Oukarroum, M'Barek Amjoud, Youssef Zeroual, and Abdellatif Barakat*

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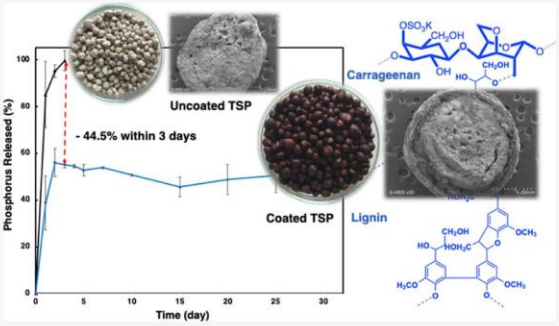
ABSTRACT: A new coated slow-release triple superphosphate (TSP) fertilizer was developed using formulations based on lignin (L) derived from olive pomace (OP) and a κ-carrageenan (C) biopolymer, and different plasticizers were added: glycerol (G) and polyethylene glycol 200 (P200) and 2000 (P2000). The effect of the type and molecular weight of the plasticizer on the physicochemical properties of the composites and phosphorus (P) release was investigated. The results showed a slight improvement in the thermal stability of the LC composite upon the addition of polyethylene glycol, while the hydrophobicity decreased. The addition of the plasticizers also decreased the elasticity of all the films except for P2000. The coating materials decreased the P release from 100% within 3 days for uncoated TSP to 55−69% within 30 days for coated TSP. However, the LC plasticizer formulations did not decrease P release compared to the LC formulations.



1. INTRODUCTION

Phosphorus (P) is an essential macroelement required for plant nutrition. It is usually the primary limiting factor because the P in soils is in chemical forms that are unavailable to plants.[1,2] Because of the continuous increase in the world population, the use of P fertilizers has become increasingly important to satisfy the global food demand. One way to enhance P fertilizer efficiency is to use controlled-release fertilizers (CRFs). CRFs show many advantages over the conventional type. This new generation of fertilizers allows progressive and continuous nutrient diffusion to be synchronized with crop requirements and ensures nutrient supply for a long time throughout the plant's growing cycle. In addition, the plants benefit from these nutrients without osmotic stress and root and leaf burn defects caused by excessive salt levels. CRFs alleviate nutrient loss and minimize the potential negative effects associated with over-dosage.[3] They can also reduce the costs related to the fertilizer quantity and labor. CRFs can be physically prepared by coating and encapsulating water-soluble fertilizers using polymeric membranes, which act as physical barriers and reduce the dissolution rate of nutrients. To fulfil the market demand, the coating materials used should be inexpensive and should exhibit good coating properties, such as film formation and biodegradation. Because of their promising properties, biobased polymers have received considerable attention as coating materials recently. Lignin (L) is an abundantly available biopolymer derived from wood-pulping processes, with a global annual production of approximately 100 million tons.[4] In addition, it is renewable, biodegradable, relatively hydrophobic, and rich in carbon.[5] Commercial lignin has been studied as a potential coating agent for mineral fertilizers and showed promoting results in term of nutrient control release.[5−7] κ-carrageenan (C) is also a promoting biopolymer for fertilizer coating. It is extracted from red seaweeds and characterized by high water absorption (WA) capacity and film-forming property.[8,9] Plasticizers are incorporated into fertilizer-coating formulation to improve the flexibility of films and to enhance the mechanical properties of the coating shell. Glycerol is one of the most commonly used plasticizers because of its high plasticizing capacity and thermal stability. It is relatively safe and biodegradable and is used as a food additive.[10] Many studies have shown that glycerol improved the flexibility of films based

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on biomass.[11,12] Polyethylene glycol (PEG) is a less-hydrophilic plasticizer than glycerol. It is known to be a nontoxic, biocompatible, nonimmunogenic, nonantigenic, and biodegradable plasticizer.[13] Qussi and Suess[14] showed that the addition of PEG increased the elongation at break (EB) (fracture strain) of free shellac films. Nekhamanurak[15] and Yuan[16] also reported an increase in the EB of poly(lactic acid)−$CaCO_3$ nanocomposites and cellulose acetate films, respectively, plasticized by PEG.

To the best of our knowledge, the effect of different plasticizer types and molecular weights on the properties of lignin−carrageenan blend films has not been reported thus far. We hypothesized that the addition of plasticizers would improve the elasticity and plasticity of the coating materials. Consequently, the shell could resist the internal pressure created inside the core when in contact with water, and P would be released slowly without the shell being destroyed. Therefore, in the present work, a series of films based on lignin derived from olive pomace and carrageenan in the presence of three plasticizers (glycerol, PEG 200, and PEG 2000) were prepared using a solution-casting method. The resulting blended films were evaluated for their structure, morphology, thermal behavior, surface properties, mechanical properties, and WA. The impact of plasticizer addition on P release from different coating formulations was also evaluated.

2. EXPERIMENTAL SECTION

2.1. Materials. The lignin was extracted from raw olive pomace (OP) biomass collected from a Moroccan olive press (Tadla region) via the alkali method according to our previous work.[17] Its elementary composition was estimated to be 58.24 ± 0.01% C, 7.89 ± 0.03% H, and 28.05 ± 0.07% O, and the C/N ratio was 32.54. Kappa carrageenan (CAS: 1114-20-8), glycerol (CAS: 56-81-5, M_w = 92.09 g/mol, d = 1.25), polyethylene glycol 200 (M_w = 200 g/mol, d = 1.125, CAS: 25322-68-3), and polyethylene glycol 2000 (M_w = 2000 g/mol, CAS: 25322-68-3) were all purchased from Sigma-Aldrich (France). Granular triple superphosphate (TSP) (46% P_2O_5), was offered by the OCP Group, Morocco.

2.2. Preparation of Formulations and Polymer-Based Films. Formulation and composite films based on lignin (L) and κ-carrageenan (C) with three plasticizers, glycerol (G), PEG 200 (P200), and PEG 2000 (P2000), were prepared. In a typical procedure, 15% of κ-carrageenan, previously prepared (0.5 w/w %) under constant stirring for 2 h at room temperature, was mixed with 55% (w/w) black liquor with a concentration of 33.34 g lignin/l obtained after alkali treatment of olive pomace. The mixture was homogenized, and then, 30% plasticizer was added under stirring overnight at room temperature. The choice of 30% plasticizers was made for two reasons: (i) in previous studies, Basiak et al.[18,19] tested different ratios of plasticizer/polysaccharide (glycerol/starch) and concluded that 30% plasticizer is the minimum concentration needed to produce ductile and nonbrittle films and (ii) we doubled the percentage of the plasticizers compared to carrageenan to study the effect of plasticizers without the effect being masked by the effect of carrageenan. For comparison, formulations based on 20% κ-carrageenan and 80% (w/w) without the plasticizer were prepared by a similar procedure. The composite films were prepared by casting the mixtures in square Petri dishes (12 × 12 cm^2) and dried overnight at 40 °C.

2.3. Characterization of the Composite Films.

2.3.1. Morphology and Thickness of the Films. The morphology of the composite films was assessed by scanning electron microscopy (SEM, Hitachi S4800) using a photoelectric detector (acceleration voltage of 2 kV). The thickness of the films was measured using an electronic digital micrometer. Five measurements were made on each test sample. The mean thickness and standard deviation were calculated.

2.3.2. Film Hydrophobicity. The dynamic contact angle (CA) measurements of different lignin/carrageenan/plasticizer films were carried out with a CA goniometer (Digidrop, GBX, France) equipped with a high-resolution video camera (CDD, 25 frames/sec) and an image GBX software analyzer.[20,21] Measurements were performed at room temperature by deposition of ∼3 μL of ultrapure water droplets on the surface of each film (0.5 cm × 2 cm) using a microsyringe.

2.3.3. Mechanical Properties of the Films. The mechanical properties of the composite films were assessed using tensile tests (TA. XT plus). The sample specimens were cut into rectangular bars (80 × 10 × 0.24 mm^3). Measurements were carried out at room temperature with a clamp speed of 5 mm/min,[17] in which the elastic modulus (EM), tensile strength (TS), and EB were determined. Three replicates were analyzed, and the results are reported as average values with standard deviations.

2.3.4. FTIR Analysis of Raw Materials and Films. FTIR spectra of different formulation composites were recorded using a Tensor 27 apparatus instrument with an ATR accessory. The spectra were obtained in the absorbance mode at a resolution of 4 cm^{-1} and an accumulation of 16 scans in the spectral range between 4000 and 400 cm^{-1}.

2.3.5. Thermogravimetric Analysis of the Films. Thermogravimetric analysis (TGA) was performed with a Mettler Toledo instrument at a heating rate of 5 °C/min from room temperature to 900 °C under a nitrogen flow rate of 50 mL/min as the purge gas.

2.4. Preparation and Characterization of TSP Fertilizer Coatings. The TSP fertilizer granules were coated in a rotary drum developed in our laboratory and described in our previous work.[17] The coating process was carried out as follows. First, an average particle size of the granular TSP fertilizer of 2−3 mm was selected using a sieve with an appropriate pore diameter. Fifty grams of TSP granules was added to the rotary drum, and then, 21.5 g of different formulations based on preprepared lignin−carrageenan/plasticizers was fed into the rotary drum with a spray nozzle at regular time intervals. After the spray coating was completed, the coated granules were dried using a hot air stream (65 °C).

2.4.1. Morphology and Thickness of TSP Coatings. The surface and cross-section morphology and thickness of the coatings were investigated using SEM, as previously described in Section 2.3.1. For thickness measurements, the granules were split in half and three measurements were performed in different areas of each sample.

2.4.2. Hygroscopicity of Uncoated and Coated TSP. To confirm the water-retention capacity of the different coated layers on the fertilizer, coated TSPs previously oven-dried under vacuum at 50 °C in the presence of P_2O_5 were exposed to two relative humidity levels, 20 and 60%, in humidity-controlled rooms for 3 days.[6] The swollen coated TPS was weighed every 24 h, and the water absorbency (g/g) was calculated using eq 1. Triplicate results were reported with standard deviations.

$$W_A = \frac{W_c - W_d}{W_d} \quad (1)$$

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where W_A is the water absorbency, W_s is the weight of the swollen fertilizer (g), and W_d is the weight of the dry fertilizer (g).

2.5. Slow-Release Behavior of Coated TSP in Water. A total of 0.25 g of fertilizers was immersed into 50 mL of distilled water in conditioned glass bottles under ambient conditions. After 1, 2, 3, 4, 5, 7, 10, 15, 20, 24, and 30 days of immersion, 1 mL of the supernatant was removed from the different solutions for analysis of the released phosphorus, and to maintain a constant volume, 1 mL of distilled water was added to the bottle. The amount of P released was quantified using the colorimetric molybdenum vanadate method.[22] The phosphorus release at each time point was obtained by the equation detailed in our previous work.[17] Three replications were performed for each type of coated TSP.

2.6. Data Analyses. Analysis of variance (ANOVA), mixed models, and correlation matrices among treatments were performed using R version 3.4.2. The effect of formulation on CA, EM, TS, and EB was tested by one-way ANOVA. The effect of formulation and time on P release was analyzed using mixed models (Package: lme4). If significant differences were found, Tukey (for ANOVA) and Emmeans (for mixed models) post hoc tests were used for pairwise multiple comparisons ($p < 0.05$). Correlations between the film and coated TSP characteristics were analyzed using a correlation matrix.

3. RESULTS AND DISCUSSION

3.1. Characterization of Lignin−Polysaccharide Composites. The micrographs (Figure 1) reveal no difference between LC films with or without the plasticizers. Nevertheless, the LCG formulation showed a slight additional layer on the surface that may be associated with the glycerol plasticizer and could produce a less-porous surface.[23] The thickness of the different films prepared was 241 ± 43 μm.

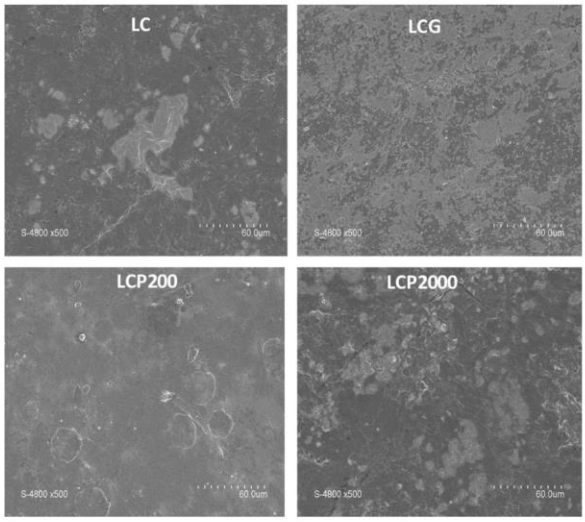

Figure 1. SEM of composite films: lignin and carrageenan (LC)/glycerol (LCG), PEG200 (LCP200), and PEG200 (LCP2000).

FTIR spectroscopy was also used to eventually identify specific interactions between the lignin, carrageenan, and plasticizers. Figure 2 shows the FTIR spectra of lignin, carrageenan, glycerol, PEG 200, PEG 2000, and composites in the range of 500−4000 cm^{-1}.

Figure 2A presents the IR spectra of κ-carrageenan powder. The characteristic band of sulfate esters (S=O) is assigned to the absorption band at 1242 cm^{-1}. The adsorption bands at 1072 and 923 cm^{-1} correspond to the presence of the C_3−O−C_6 bridge of 3,6-anhydrogalactose, and the band at approximately 848 cm^{-1} indicates the presence of C−O−SO_3 on C_4 of galactose (Figure 2A).[24−26] FTIR spectra of several major absorption bands representing the typical structure of lignin are shown in Figure 2B. The examination of spectra reveals absorption peaks located at approximately 2925 and 2840 cm^{-1}, attributed, respectively, to the asymmetric and symmetrical stretching vibrations of the C−H group of the alkyl chains in aliphatic structures, both of which are attributed to fatty acids.[27] The peaks at 1460 cm^{-1} indicate the existence of C−H (deformation in $-CH_3$ and $-CH_2$). The appearance of peaks attributed to carbonyl groups (C=O) at 1705 and 1650 cm^{-1} indicates that C=O bonds are nonconjugated and conjugated with aromatic rings, respectively.[28,29] Another band observed at 1270 cm^{-1} corresponds to the vibration of the Lignin-guaiacyl group, while the band observed at 1370 cm^{-1} is attributed to lignin-syringyl, which is in good agreement with results reported by Ye et al.[30] and Gutierrez.[28] The spectra of pure glycerol (Figure 2C) show several bands; C−H stretching vibrations give rise to two bands at 2932 and 2879 cm^{-1}.[31] The bands observed at 850 and 995 cm^{-1} can be attributed to vibrations of the skeleton C−C bonds. The bands at 1045 and 1117 cm^{-1} correspond to stretching of the C−O linkage and to stretching of C−O, respectively.[32] The band at 3268 cm^{-1} is attributed to O−H stretching vibrations, and the band at 925 cm^{-1} is attributed to C−O−H stretching vibrations.[33] The FTIR spectra of P200 and P2000 (Figure 2D,E) show several specific peaks: the band at 3400 cm^{-1} is attributed to the stretching vibration bands of the hydroxyl groups existing on the surface of the polymer matrix, and the peak at 2900 cm^{-1} corresponds to C−H stretching of the alkyl chain of the polymer. The peaks in the range of 1450−1292 cm^{-1} are assigned to C−H scissoring and bending; the peak at 1250 cm^{-1} corresponds to C−O stretching of the alcohol group, and the peak at 1100−1060 cm^{-1} reveals the presence of the C−O−C ether group.[34] For LC, LCG, and LCP (200−2000) composite films, as expected, characteristic bands of lignin (2925, 2840, 1705 cm^{-1}), carrageenan (923 cm^{-1}), glycerol (3268, 1045 cm^{-1}), and PEG (1060, 1100, 1250 cm^{-1}) were all identified (Figure 2F−I). The intensity of the band observed at 3268 cm^{-1} tends to increase with the addition of plasticizers.

Figure 3A shows that thermal degradation of the LCP200 and LCP2000 composite films was similar but was different from that of the LC and LCG composite films. Generally, for the different composite films, we observed two endothermic peaks with a maximum at 25−200 and at 200−500 °C. The first step (25−200 °C) associated with a mass loss ranging from 9 to 18 wt % is attributed to the elimination of physisorbed water on the external surface and dehydration of the intern layer. The other relatively large endothermic peak observed in the temperature range from 200 to 500 °C with a major decomposition step corresponds to the decomposition of organic matter. Comparing all samples in the first range of 25−110 °C allowed observation of the loss of water, which was the highest for LC (12.19%), followed by LCG (9.87%) and the LCP2000 composite (7.66%), whereas the LCP200 sample had the lowest water content of only 6.86%. A higher evaporation temperature of water in films shows a stronger interaction between the film and water.[35] The stronger water retention in the LCG compared

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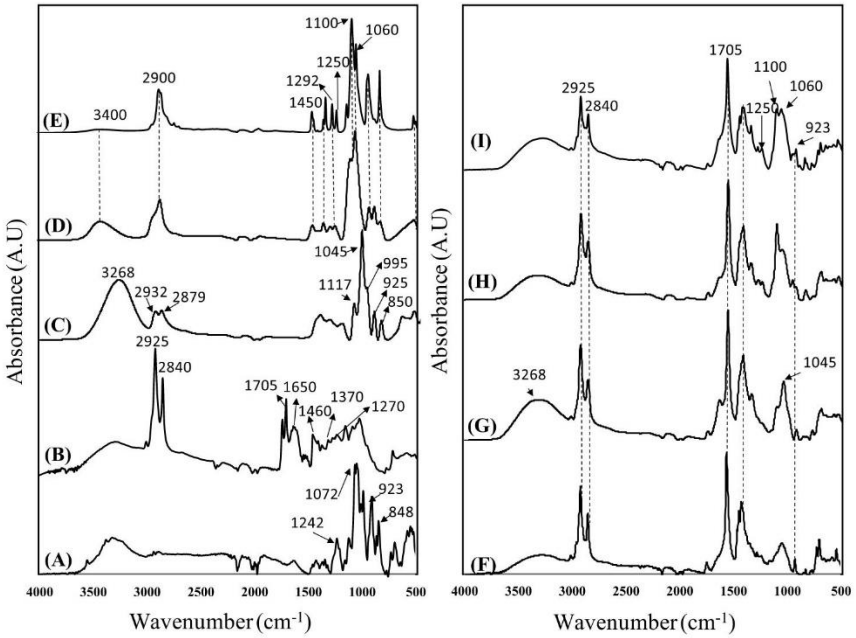

Figure 2. FTIR spectra of (A) κ-carrageenan powder: C, (B) lignin powder: L, (C) liquid glycerol: G, (D) liquid PEG 200: P200, (E) powder PEG 2000: P2000, (F) LC film, (G) LCG film, (H) LCP200 film, and (I) LCP2000 film.

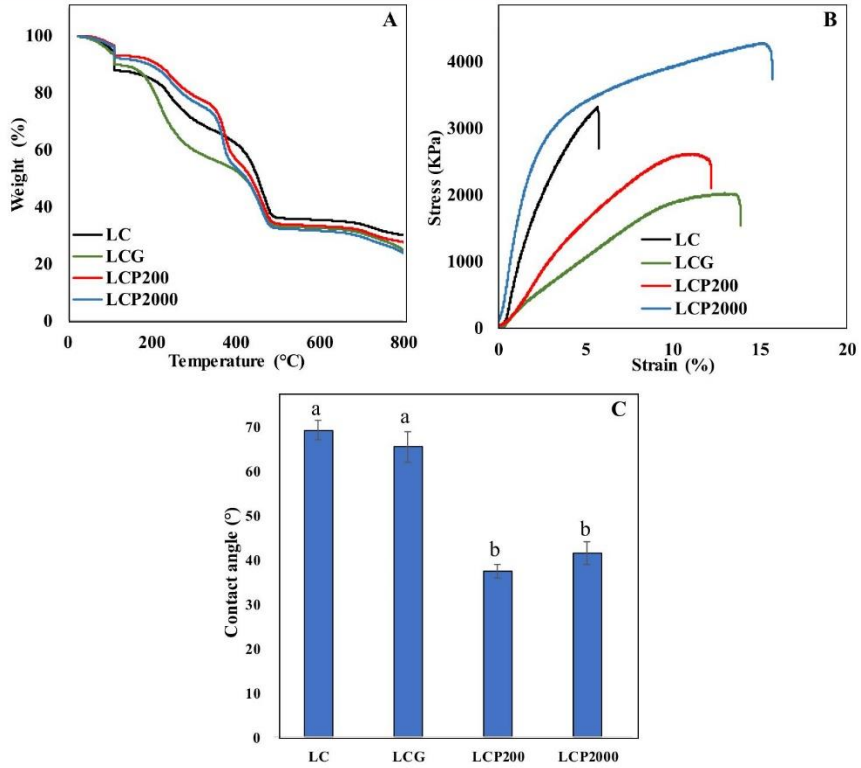

Figure 3. (A) TGA, (B) mechanical properties, and (C) CA measurements of different composite films based on lignin and carrageenan (LC)/glycerol (LCG), PEG200 (LCP200), and PEG200 (LCP2000), $n = 3$.

to the LCP films was probably due to the hydrophilicity of glycerol[10] compared to PEG. However, the samples with the lowest weight loss in the range of 200−400 °C were LCP2000 and LCP200, followed by LC, and the largest weight loss was that of the LCG-based composites. Faradilla et al.[10] also showed that glycerol reduced the film thermal stability.

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Figure 3B and Table 1 show the TS, EB, and EM of the composite films. It was found that the plasticizer type and the degree of cross-linking impacted the mechanical properties of the LC composite films. Table 1 shows a significant difference in the EM and TS ($p < 0.05$), while no significant difference was observed in the EB ($p > 0.05$) between different composite films. The addition of glycerol and PEG200 to the LC formulation decreased the EM from 1191 to 143 and 887 kPa, respectively, while an increase was observed for PEG 2000 (1276 kPa). The TS of the composite films varied between 1878 and 4296 KPa. Among all samples, LCP2000 exhibited the highest TS, while LCG displayed the lowest value (LCG < LCP200 < LC < LCP2000). The blending of lignin with carrageenan in the presence of plasticizers increased the EB of the films. The EB ranged between 9.37 and 16.85% in the order LC < LCP2000 < LCG = LCP200 (Table 1).

Table 1. EM, TS, and EB of the Films Lignin and Carrageenan (LC)/Glycerol (LCG), PEG200 (LCP200), and PEG200 (LCP2000) ($n = 3$)[a]

	EM (KPa)	TS (KPa)	EB (%)
LC	1191 ± 356^{a}	3674 ± 318^{ab}	9.37 ± 1.99^{a}
LCG	143 ± 60^{b}	1878 ± 209^{c}	16.85 ± 3.68^{a}
LCP200	887 ± 33^{ab}	3238 ± 192^{a}	16.85 ± 3.60^{a}
LCP2000	1276 ± 304^{a}	4296 ± 161^{b}	16.65 ± 4.40^{a}

[a]a−c: Within a column, different letters indicate significant differences between formulations ($p < 0.05$).

The TS of the LCP2000 film was higher than that of LCP200, probably because of the higher molecular weight of P2000 (2000 g/mol).[36] This result is in agreement with the study reported by Cao et al.,[37] who showed an increase in the TS with an increase in the molecular weight of PEG. However, Yuan et al.[16] found that the PEG molecular weight had no significant effect on TS. Aadil et al.[36] used lignin (L) derived from acacia wood and alginate (A) and PEG4000 (P4000) and glycerol (G) as plasticizers for the preparation of LA, LAP4000, and LAG composites (L/A ratio: 1/4). The authors reported that the LAP4000 and LAG composite films had higher TS values of 625 and 569 kPa, respectively, than LA, with a value of 413 kPa. In comparison, the LC, LCP200, LCP2000, and LCG composites (this study) had higher TS values than LA, LAP4000, and LAG.[36]

Figure 3B shows an elastic zone in LC/plasticizer composites, which was significantly different among the different formulations. In comparison with the other composites, the LCP2000 composite showed an additional plastic zone and a higher EB. The elasticity and plasticity give the film the capacity to extend before breaking.[38] This property could be important for a coating formulation to resist pressure without breaking during swelling.[39] The addition of carrageenan to lignin in the presence of plasticizers enhanced the EB of composite films and sometimes their Young's modulus and TS. Faradilla et al.[10] reported that glycerol increased the elasticity of nanocellulose films but reduced the TS. Our results showed that glycerol decreased both the TS and elasticity of the LC film. Our results for P200 are in accordance with the results of Qussi and Suess[14] who reported that the addition of PEG decreased the EM of free shellac films. Indeed, the best mechanical properties were obtained by LC and LC2000: high EM, high TS, and high EB, along with a plastic behavior. These properties could be interesting for mineral fertilizer-coating formulations.

Contact angle measurements were performed to investigate the surface properties and the effect of the plasticizer type on the hydrophobicity of lignin/carrageenan composites. The structure and composition of the film surface could be affected by the addition of a plasticizer.[21] The results show that plasticized LCP200 and LCP 2000 films exhibited significantly lower CAs than the LC films without a plasticizer. The CA of the LC/plasticizer films ranged between 36.1 and 64.32° and decreased in the following order: LC ≥ LCG > LCP2000 ≥ LCP200 (Figure 3C). The slight decrease in the CA for LC in the presence of glycerol could be associated with the hydrophilic behavior of glycerol. This result is in accordance with that of Karbowiak et al.,[21] who reported that the presence of glycerol in carrageenan formulation decreased the surface hydrophobicity. The CA of LC also decreased by the addition of PEG. Yuan et al.[16] also reported that PEG increased the hydrophilicity of the film. However, no significant difference in the CA was observed between LCP200 and LCP2000. Faradilla et al.[13] studied the effect of PEG at different molecular weights (400, 1000, 2000, 4000, and 8000 g/mol) as plasticizers on the CA of nanocellulose films. They found no difference linked to the variation in the PEG molecular weight. Our results are also in accordance with those of Yuan et al.,[16] who reported that PEG-plasticized films exhibited lower CAs compared to cellulose acetate films without a plasticizer because PEG increases the hydrophilicity of the film. They argued that no significant effect of PEG molecular weight on CA measurements was observed.

3.2. Coated TSP Fertilizer Properties. Figure 4 shows a visual image of the coated TSP granules and uncoated TSP. Coated TSP granules were brown and completely covered by the film coating.

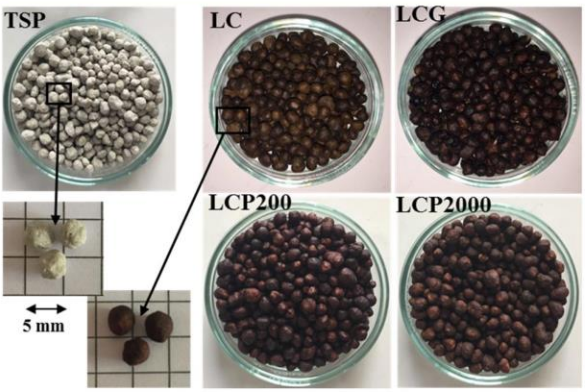

Figure 4. Real image of uncoated and coated TSP with lignin and carrageenan (LC)/glycerol (LCG), PEG200 (LCP200), and PEG200 (LCP2000).

Figure 5 shows the cross-sections (A,B) and whole granules (C,D) of uncoated and coated TSP fertilizers by SEM. Micrographs show good adhesion between the fertilizer and coating. The thickness of the coating was 218 ± 62 μm.

The WA of all formulations was also measured. Figure 6 shows that the WA increased with increasing humidity (20−60% RH) and with time (1, 2, and 3 days). The uncoated TSP fertilizer exhibited lower values of WA, while the coated TSP with LC and LC plasticizers presented the highest values. The hygroscopicity of the TSP granules was ranked in the following order: TSP < LCP200 < LCP2000 < LCG. Faradilla et al. argued

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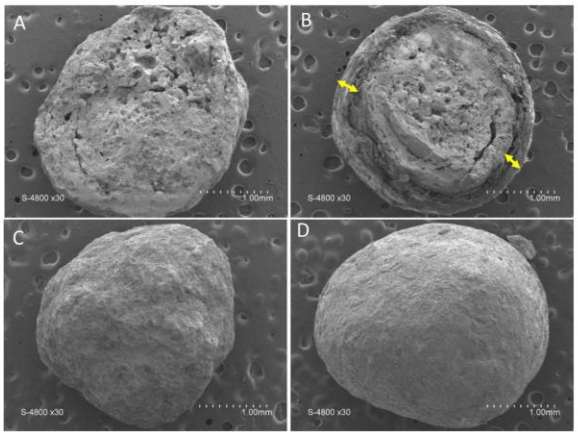

Figure 5. SEM of the cross-section of (A) uncoated TSP fertilizer, (B) LC-coated TSP and the whole granule, (C) uncoated TSP, and (D) LC-coated TSP.

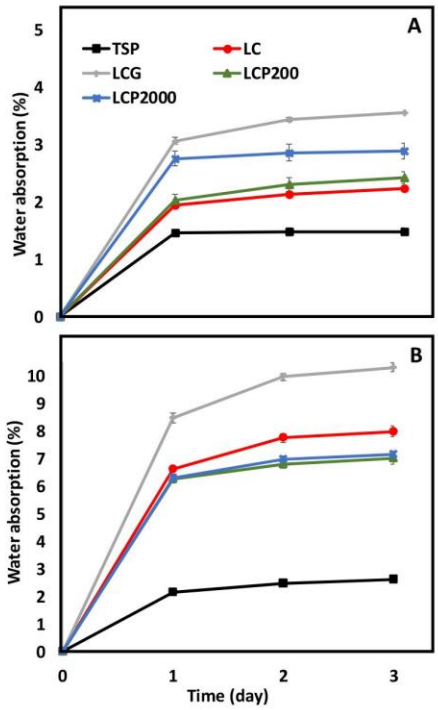

Figure 6. WA of uncoated and coated fertilizers over time at different relative humidity levels: (A) 20 and (B) 60% with lignin and carrageenan (LC)/glycerol (LCG), PEG200 (LCP200), and PEG200 (LCP2000), $n = 3$.

that glycerol increased moisture sorption.[13] PEG is less hydrophilic than glycerol, which is probably why the WA of LCP is lower than that of LCG.[13] In addition, plasticizers with a low molecular weight [M_w (glycerol) = 92.09 g/mol] occupy the intermolecular spaces between polymer chains and increase the free volume,[15] which probably boosts the composite swelling. Faradilla et al.[10] also observed the same phenomenon observed in another work with a glycerol-plasticized banana pseudostem nanocellulose film. In our work, the WA at 60% RH (3 days) of LC plasticizers@TSP was found to be higher than that of LC@TSP. An increase in WA of 204, 293, 167, and 172% was observed for TSP coated with LC, LCG, LCP200, and LCP2000 compared to that of the uncoated TSP granule. This high WA of the LC plasticizers@TSP could be related to the low degree of cross-linking between the carrageenan and lignin molecules in the presence of plasticizers.

3.3. Slow-Release Behavior of Phosphorus from Coated TSP Fertilizers. To evaluate the performance of the composite films from different formulations developed in this study, the release of P from uncoated TSP and coated TSPs with different formulations was studied in water over 30 days. TSP showed a rapid P release, with 85% ± 14 and 95% ± 4 P released within 1 and 2 days, respectively, and a complete dissolution of P from TSP was reached after 3 days (Figure 7). LC with or

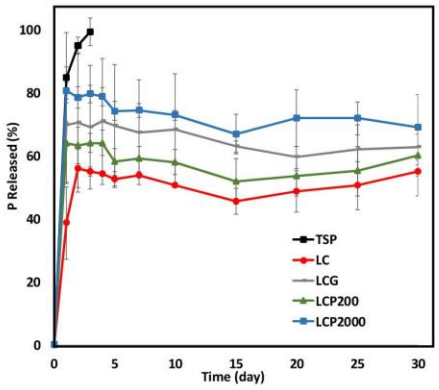

Figure 7. Release of phosphorus in water from TSP and coated TSP fertilizers with lignin and carrageenan (LC)/glycerol (LCG), PEG200 (LCP200), and PEG200 (LCP2000), $n = 3$.

without plasticizers exhibited the slowest P release. The amounts of phosphorus released at day 1 from LC/plasticizers@TSP ranged from 39 to 81%. TSP@LC exhibited the lowest value, while LCP2000@TSP exhibited the highest value. The P release from different coated TSP granules with different formulations was ranked in the following order: LC < LCP200 < LCG < LCP2000. After 2 days, LC@TSP released more P, reaching 56% ± 6, while LCP200@TSP, LCG@TSP, and LCP2000@TSP stabilized at 71% ± 22% ± 6 and 79% ± 3, respectively. There was no significant effect of plasticized formulations on the release behavior of P from TSP fertilizers. The LC plasticizer formulations did not decrease the release of P compared to the LC formulation. This is most likely due to the hydrophilic behavior of the plasticizers.[13] The transition from the linear release stage to a constant phase started at day 2 for LC@TSP and at day 1 for the others.

From the second day, the release behavior curve of P from all coated TSPs stabilized, and the amount of P released remained the same throughout 30 days. Rotondo et al.[40] and Garcia et al.[6] observed the same phenomenon with simple and TSP, respectively, coated by lignin-based formulations. Rotondo et al.[40] explained this result by the fact that using lignin as coating materials limits the solubilization of $Ca_3(PO_4)_2$ and by the interactions between salts in the original fertilizer.

P release is negatively correlated with EM ($r = -0.2, p = 0.62$), while it is strongly positively correlated with EB ($r = 0.91$, $p = 0.001$) (Table 2). In relation to the elasticity of the coating materials, if the coating material is elastic, the shell is able to resist the internal pressure created inside the core upon contact

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Table 2. Correlation Matrix between the Properties of Composite Films and Coated TSP[a,b]

	P-release	EM	TS	EB	CA	WA
P-release	1					
EM	−0.2	1				
TS	−0.02	**0.98****	1			
EB	**0.91****	−0.43	−0.28	1		
CA	−0.61	−0.35	−0.44	−0.64	1	
WA	**0.73***	−0.58	−0.43	0.61	0.09	1

[a]Film properties: EM, TS, EB, and CA. Coated TSP properties: P release within 1 day and WA (water absorption at RH 20% within 1 day). [b]*p*-value for correlations significance: (***) <0.001; (**) <0.01; and (*) <0.05.

with water, and P is released slowly without destruction of the shell. A moderately negative correlation between P release and CA was also revealed ($r = -0.61$, $p = 0.1$). This phenomenon could be explained by the fact that when the CA is large, the coating material is hydrophobic, and then, the affinity between the layer and water is weak. This lack of affinity prevents the penetration of large quantities of water inside the fertilizer core and then decreases the dissolution of TSP. The opposite could explain the strong correlation ($r = 0.73$, $p = 0.03$) between P release and WA. The same correlations between lignin−polysaccharide TSP coating properties and P release were reported in our previous work.[41] From these data and the discussion, we concluded that the LC formulation is the most efficient coating for the mineral TSP fertilizer because of its high EM and high CA and, consequently, the slow release of P.

4. CONCLUSIONS

This work reports the valorization of lignin derived from olive pomace biomass (OP). OP lignin was used with κ-carrageenan polymers as coating formulations for mineral TSP granules. Different formulation composites were successfully synthesized using the casting method in the presence of three different plasticizers. The effect of different plasticizer types on the structural, thermal, mechanical, and surface properties of plasticized lignin−carrageenan film composites was also evaluated and compared. The results showed that the hydrophobicity of the composites decreased with increasing plasticizer addition. The addition of plasticizers also decreased the elasticity of all films except PEG 2000. The use of these formulation composites as coating materials for TSP fertilizers to decrease the release of phosphorus was also investigated in water. The coating materials decreased the P release from 100% within 3 days for uncoated TPS to 55−69% within 30 days in the case of the coated TSP granules. However, the type and molecular weight of plasticizers had no significant effect on phosphorus release in water.

AUTHOR INFORMATION

Corresponding Author

Abdellatif Barakat − *IATE, Montpellier University, INRAE, Agro Institut, 34060 Montpellier, France; Mohammed VI Polytechnic University, 43150 Ben Guerir, Morocco;* orcid.org/0000-0003-4196-4351; Email: abdellatif.barakat@inrae.fr

Authors

Saloua Fertahi − *IATE, Montpellier University, INRAE, Agro Institut, 34060 Montpellier, France; Mohammed VI Polytechnic University, 43150 Ben Guerir, Morocco; IMED-Lab, Faculty of Science and Technology, Cadi Ayyad University, 40000 Marrakesh, Morocco; Eco&Sols, Montpellier University, CIRAD, INRAE, IRD, Agro Institut, 34060 Montpellier, France*

Isabelle Bertrand − *Eco&Sols, Montpellier University, CIRAD, INRAE, IRD, Agro Institut, 34060 Montpellier, France*

Mohamed Ilsouk − *Mohammed VI Polytechnic University, 43150 Ben Guerir, Morocco*

Abdallah Oukarroum − *Mohammed VI Polytechnic University, 43150 Ben Guerir, Morocco*

M'Barek Amjoud − *IMED-Lab, Faculty of Science and Technology, Cadi Ayyad University, 40000 Marrakesh, Morocco*

Youssef Zeroual − *Situation Innovation, OCP Group, 24025 El Jadida, Morocco*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.iecr.0c03143

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

L	lignin
C	carrageenan
G	glycerol
P200	polyethylene glycol 200
P2000	polyethylene glycol 2000
LC	lignin−carrageenan
LCG	lignin−carrageenan−glycerol
LCP200	lignin−carrageenan−PEG 200
LCP2000	lignin−carrageenan−PEG 2000
EM	elastic modulus
EB	elongation at break
TS	tensile strength
CA	contact angle
WA	water absorption

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