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Characteristics of cassava starch (*Manihot esculenta*) and its use as raw material for the development of technologies in agricultural production

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Graphical Abstract

Abstract. Starch is an important raw material for the chemical, pharmaceutical, textile, and mainly food industries due to its desirable functional properties, whether native or modified. In addition, it is considered the main energy-storage carbohydrate. Allowing you to present advantages such as low-cost material, abundance, and availability. Therefore, compared to synthetic polymeric materials, it contains hydroxyl groups that give it hydrophilic properties. Amylose and amylopectin have an important role in the composition, since they constitute the majority of the starch, which influences properties such as crystallinity, viscosity, retrogradation, gelation, and stickiness. These properties are essential to give this raw material an industrial use, either in food or in the production of biodegradable films.

Keywords: Carbohydrate, starch, polymeric materials, amylose, amylopectin, macromolecule.

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Content

1. Introduction

Agriculture is an essential activity for the supply of food and from which sustenance is provided to almost two-thirds of the people in extreme poverty in the world, some 750 million, who are in a state of vulnerability in their security by the different factors that affect agricultural production today. In Colombia, there are various factors that cause a high yield of crops compared to other countries, an important aspect is the little research and technological development adapted to the current situation of the country, the low innovation, and the use of new technologies (MADR, 2019). It has been shown that it presents a limitation due to the scarcity of inputs, particularly fertilizers, impacting production, it is considered that its results are achieved by integrating various factors such as knowledge of the nutritional requirements of plants, soil fertility, characteristics, properties of fertilizers, as well as the technology of application of these materials, which is decisive for increasing the efficiency of the nutritional supplement to the soil-plant system and which is an aspect very little attended by producers (Luz et al., 2010). The growth of the world population, the increase in production costs, and food prices make productive systems vulnerable, which repeatedly promotes the search for scientific and technological solutions to strengthen food security, mainly addressing the availability of nutrients in the soil for crops (Montoya, 2021). However, the efforts to increase productivity have led to the implementation of practices of excessive use of fertilizers, generating the degradation of resources, mainly the soil. Therefore, it is necessary to adopt alternatives and articulate strategies that, in addition to increasing crop production, are sustainable and allow the protection of renewable and non-renewable resources (FAO, 2015). Cassava is a product that forms an important part of the agricultural sector, it is cultivated in the 32 departments of Colombia (MADR, 2019) and large amounts of waste material are generated in the post-harvest stage without having to a specific study, it is known that it occupies an important place and is part of 25 % of the 9.76 million tons of roots and tubers lost and wasted in the country (DNP, 2016). The area planted with cassava in the country has been increasing significantly so that by the year 2020 around 2.5 million ha were planted for a national production of 2.481.183 tons (UPRA, 2020). Nearly 60 million tons of starch are extracted annually from a wide variety of crops in the world, of which 10 % is obtained from cassava root; its application in the food, pharmaceutical, textile, chemical, construction, and agricultural industries make this product attractive and the object of growing studies. An alternative to make the use of fertilizers efficient and guarantee the reduction of losses in their application is the use of vehicles that guarantee the availability of nutrients for plants. Thus, cassava biopolymer is an important alternative that reduces the risk of contamination due to the efficiency it provides in the application of fertilizers (Montoya, 2021). On the other hand, the implementation of new technological and innovative tools makes the use of crop residues favorable for the industry, particularly cassava crops; becoming an important contribution to sustainable development since the economy has been transformed and globalization demands more competitive and sustainable proposals (Aristizábal and Sánchez, 2007). In this sense, efforts and research have been carried out to prepare starch-based biodegradable biopolymers, which not only serve as a mechanism for the slow release of fertilizers, but can also become nutrients in the life cycle of many microorganisms, given their compatibility with the environment, in such a way that it would become organic fertilizer in the soil (Nafchi, 2013). Agricultural production systems are highly vulnerable to the effects of climate change due to the low possibility of implementing adaptation measures to face the occurrence of extreme weather events. In the economic sphere, it is very likely that the agricultural sector will be the most affected by these effects, which will complicate efforts to reduce poverty and affect food security (Ramírez et al., 2014).

The yucca root is a tuber that belongs to the *Euphorbiaceae* family, which is characterized by producing a large amount of milky secretion because its structure contains laticiferous vessels and galactocytes, in addition to being of Amazonian origin, within the genus *Manihot*, and there are around 98 species where the one that has the greatest relevance for its cultivation and economy is cassava; This plant presents an allogamous reproduction and due to its genetics, it is heterozygous. For this reason, its planting is based on reproduction by cuttings and not by seeds (Suárez and Mederos, 2011). The main use of this plant is based on the consumption of the tuber because it is where the main components such as starch, carbohydrates, and sugars, among others, accumulate. Cassava is a competitive product in four markets taking into account the possible uses of this tuber, the most common and well-known being to process it for direct consumption in conventional homes, a direct source in the industry to transform it into dry flour, raw material for the production of concentrates or feed for animals (Patiño et al., 2002), **Table 1** shows the chemical composition contained in cassava flour.

2. Cassava (*Manihot esculenta* Crantz) as a source of starch

Table 1. Percentage chemical composition of cassava flour (Sánchez et al.,2009; Patiño et al., 2022).

Amylose	Protein	Starch	Ash	Fiber	Fat
-	0.49	-	0.24	0.15	0.13
16-20	0.05-0.28	-	0.12-0.33	-	0.04-0.38
20.6-21.0	0.59-0.63	-	0.32-0.66	-	-
20.7	-	84.5	-	-	-

The greatest production and consumption of cassava is focused mainly on countries such as Paraguay, Colombia, Ecuador, Brazil, and Venezuela, the latter country being the one that has recently ventured into the production of cassava flour to replace wheat flour and reduce imports (Torres and Pacheco, 2007). However, the most consumed and important product is starch from the root, because it covers the textile and food industries, providing percentages of 0.55 protein, 0.25 fat, 1.04 fiber, and 33.40 % carbohydrates, solving problems in the human and animal diet (Coral and Gallegos, 2015).

2.1. Starch

The most important carbohydrate used to store energy is starch, because its structure is composed of a polysaccharide that is made up of glucose molecules (Ball and Morell, 2003). In addition, starch can be extracted from different raw materials such as cereals, tubers, and legumes, among them are corn, rice, sorghum, potato, yam, sweet potato, lentils, and beans, among others (Peroni, 2003). On the other hand, an essential characteristic of starch granules is that they are dense and insoluble in cold water; however, when the water is heated, the granules absorb water and the hydrogen bonds are broken, causing a release of amylose, and, in turn, generating higher viscosity, it must be taken into account that starches, depending on the source of creation, present a different type of gelatinization (Soto and Oliva, 2012). Therefore, the changes in the relationships between these two components can change the physical, chemical, and functional properties of the starch, which affects its possible industrial applications; the production of starch-based biofilms with excellent fundamental properties depends on the amylose composition in the structure because it gives it the ability to form films more easily (Young, 1984).

2.1.1. Chemical structure of starch

The chemical structure of starch is mainly constituted by carbons, hydrogens, and oxygens with the following molecular formula ($C_6H_{10}O_5$), it is known within organic compounds as carbohydrates, because it is considered a glucose polymer (Souza and Andrade, 2001). Generally, the starch structure presents two essential components such as amylose and amylopectin, which are interconnected by hydrogen bonds, these bonds are connected by the OH groups present in glucose molecules. Therefore, the main component of starch granules is amylopectin with a composition of 75 %, in addition to being a molecule of high molecular weight and

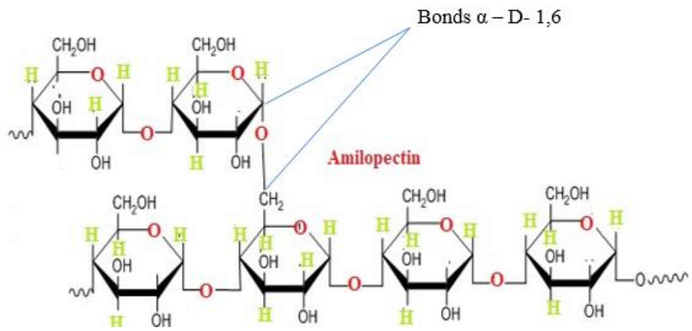

Figure 1. Chemical structure of the amylopectin molecule.

ramifications, its molecular structure in the form of ramifications makes it a similar structure to a tree, branches being the ones that form the groups of chains, this amylopectin molecule can be differentiated from amylose by its extensive ramifications that are linked by α–1,6 bonds that are located in positions every 15 – 25 units in a linear fashion, glucose, while amylose is a linear molecule with α–1,4 bonds (Soto and Oliva, 2012). **Figure 1** shows the structure of the amylopectin molecule.

According to Villarroel et al. (2018), amylose and amylopectin are the main components of starch carbohydrates, which are approximately 98 – 99 % of their dry weight, amylopectin gives characteristic properties to starch such as crystallinity, while amylose is responsible for giving amorphous shape to the granules. For this reason, crystallinity occurs thanks to the function performed by the double helices that form the branches of amylopectin, which is observed when the granules enter the presence of water and the amorphous phase is more prone to enzymatic or chemical attack. The amylose molecule is of low molecular weight and its structure is linear, formed by glucose molecules linked by α-1,4 glycosidic bonds. Its structure can be detailed in **Figure 2** (Villarroel et al., 2018).

2.1.2. Starch properties of interest

The main advantages of starch as a material include its low cost, abundance, and availability, in addition, compared to synthetic polymeric materials, starch contains hydroxyl groups that give it hydrophilic properties that amylose dissolves and amylopectin swells in the presence of water, thus starch disintegrates in water (De Carvalho et al., 2001). In addition, amylose and amylopectin play crucial functional and compositional roles in cassava starch, influencing its properties such as crystallinity, viscosity, retrogradation, gelation, and stickiness. According to what was commented by Tukomane (2007), cassava starch that has a low amylose content may present greater crystallinity, which is due to a reduced amorphous band, but the opposite happens when it has a high amylose content, it presents an instantaneous retrogradation (Rodríguez et al., 2008).

The crystallinity that starches can present depending on their origin is different in each case since they can emit different types of diffraction, whether A, B, and C, which are dependent on the structure of amylopectin with its chains and branches, due to the ex-

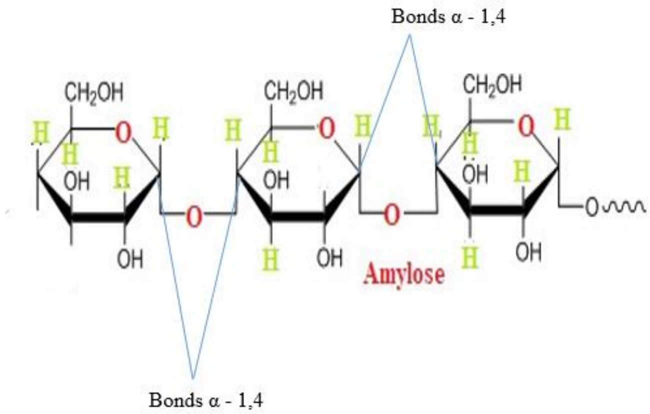

Figure 2. Chemical structure of amylose.

ternal chains of amylopectin can form double helices, which are responsible for allowing X-ray diffraction in the structure (Rodríguez et al., 2008; Rivas, 2012). Therefore, diffraction type A can be observed thanks to the short chains, while diffraction types B and C are shown by the intermediate and long chains. Continuing with what was mentioned by Rivas (2012), about the types of diffraction, it shows that a type of starch with a higher amylopectin content has greater crystallinity than another type of starch with a higher amylose content; indicating that crystallinity and branching in type B molecules are directly responsible for crystal formation.

Gelatinization is another essential property for starches, in which the intermolecular forces that act on the starch granules intervene and also depend on the content of amylose and amylopectin present, the gelatinization process in starches occurs in temperature ranges from 49 - 64 °C, basically, what happens in this process is an ordering of the granules, that is, the higher the temperature value obtained to reach gelatinization, the greater the degree of organization of the molecules in the starch granule (Rached et al., 2006).

Another important property of starch is retrogradation, which is a process that occurs when the amylose chains are solubilized during the gelatinization process, forming crystalline double helices stabilized with hydrogen bonds, this happens when the temperature decreases, therefore, it is they form three-dimensional crystalline structures of type B, which are very stable, in addition, they present a melting endotherm around 150 °C and can be resistant to enzymatic digestion (Jane and Robyt, 1984). Consequently, amylopectin molecules can also form crystallization by linking short side chains, while amylose retrogradation is an accelerated process that takes place within a few hours, while the process with amylopectin requires more time (Miles et al., 1985).

2.1.3. Conditions that limit the starch content of cassava

Starch is the most important component of cassava root, so it is expected that the quality of the products derived from it is largely determined by the quality of its starch (Westby, 2002). The starch content in a variety of cassava can vary due to the dry matter content

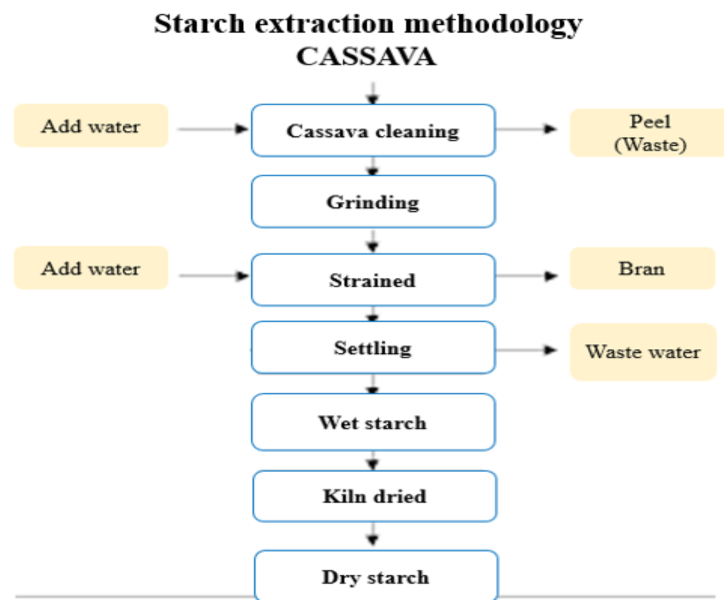

Figure 3. Cassava starch extraction based on the methodology of Alarcón and Dufour, 2002 and Torres et al., 2005.

and thickness of the shell, the yield of obtaining starch also depends on the drying conditions, preferably in the oven and not directly in the sun (Pérez et al., 2011). Other influencing factors are harvest time and the type of storage of the roots, the longer the storage time, the lower the starch content, since environmental conditions have a direct influence (Benesi et al., 2007). In **Figure 3**, the cassava starch extraction methodology can be observed.

2.1.4. Utilities of cassava starch in agroindustry

The physical and chemical properties present in starch give it important and functional features that open doors in the industry of synthetic polymers that are of natural origin such as starch. The most common natural sources of starch extraction are corn, yams, potato, wheat, and Cassava (Vanier et al., 2012). Starch is a product that has particular characteristics due to the fact that it has no odor or taste, for this reason, it is highly desired for the manufacture of sausages, breads, sauces, and dressings among many more products. There is also another type of starch called sour starch which undergoes a fermentation process and is used for the preparation of cassava bread, bonus bread, cheese bread, fritters, and others, due to the characteristic flavor that each preparation gives it (Torres et al., 2010).

3. 3. Technological innovation, biopolymers and their application in agriculture

In all types of crops, biopolymers can act as nutrient supplements in the soil, that is, they complement the availability of nutrients in said crop soils, in addition, they are used to maintain ideal climates, identify and treat different phytopathologies (Zhang et al., 2017). Taking into account what was stated by Borschiver et al. (2008), who mention that oil was the main source of raw material for the production of synthetic biopolymers, without measuring the increase in prices and the growing pollution from the exploitation of this mineral, the authorities in charge of environmental protection, raised the initiative to seek renewable sources that guaranteed the production of biopolymers in an efficient and less polluting way. For this reason, different investigations have been carried out, that present biopolymers based on natural fibers as an excellent, renewable, self-sustaining alternative for capturing and thus reducing carbon dioxide emissions in nature, during their production and transformation stage in order to increase their economic potential in the production chain. Likewise, increasing the need for development, reducing consumption, opting for sustainable solutions and products throughout their life cycle, and finding a balance between man and nature have become fundamental considerations in product development (Lemos and Martins, 2014). On the other hand, when it comes to sustainability Pereira et al. (2014), provide that the production of biocomposites from renewable raw materials such as *Copernicia prunifera* (Miller) straw, can facilitate the production of biodegradable films.

Furthermore, this study can be complemented by the one carried out by Guimarães et al. (2020), where they indicate that the biocomposites obtained from the seeds of *Moringa oleifera* Lam are an alternative with great potential for the removal of dissolved solids in water, serving for water treatment, because they carried out different tests, the method implemented with Moringa showed better results since it decreased the turbidity and color of the water.

Cassava starch is a natural polymer that is used by native people to coat their fruits and some tubers since it has no color, or odor, is not toxic, and biologically degrades, it is an economic technique and also renewable (Ruíz et al., 2009). However, this natural polymer has some limitations that affect its properties, such as rapid degradation, low resistance, and high levels of retrogradation. These properties can be improved when the starch undergoes an oxidative process since this chemical process helps to lower the viscosity level, paste clarity, increase strength, and lower gelatinization temperature (Sangseethong et al., 2010).

Taking these assertions into account (Montoya et al., 2021), in their research they developed a biodegradable coating film based on cassava starch to create greater resistance and fluidity in the crops, creating a method to polymerically coat the seeds with a polymer natural food grade and biodegradable, to become a sustainable agriculture. Similarly, a study carried out on *in vitro* cultures of marigolds, where biopolymer-based tablets were developed as a transport medium for the slow release of organic nutrients, showed favorable results in plant development (Cobo, 2014).

5.1. Slow soluble fertilizers

Within the framework of sustainable agriculture, biopolymers have intervened in the coating of mineral nutrients such as nitrogen, phosphorus, and potassium which are essential for the development of agriculture and thus counteract all the food demands that have arisen worldwide (Majeed et al., 2014). The coating of fertilizers such as urea, nitrate, or potassium chloride is made with polymers (see **Figure 4**) such as polyacrylamide which is highly hydrophilic, with the purpose of prolonged release of the supply as it comes into contact with the water contained in the soil and maintaining the nutrition as a more appropriate requirement for the crop (Shavit et al., 2002). In **Figure 5**, the conventional fertilization of a crop is observed (curve A), at a certain time between points X_1 and X_2. In the same way, a new application of fertilizer is shown in curve C, which are very conventional applications in daily agriculture to try to meet the nutritional needs of the crop in the last cycle, because a single application is not enough to consider it as loss, due to excess application, which is well above the real requirement of the crop, as observed in the shaded area under the curve (Z). Dave et al. (1999) mention that the coating of fertilizers seeks that the fertilizer application follows the dotted curve B which shows a real requirement of a crop, maintaining this application the same trend and even higher than the requirement curve.

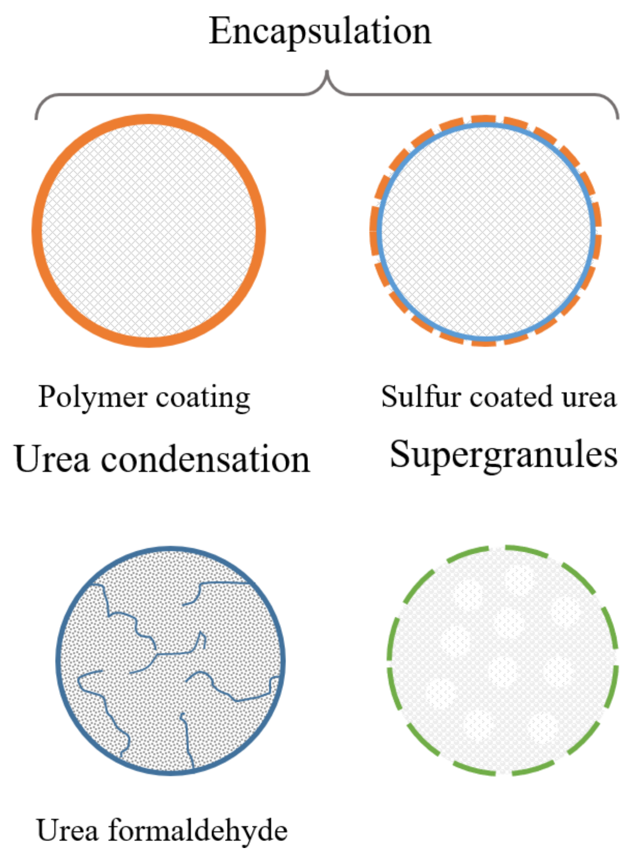

Figure 4. Diagram of different polymer matrices.

Slow-release fertilizers are those that coat the fertilizer so that it is released more slowly and lasts much longer in the soil than a conventional fertilizer (Shavit et al., 2002). These can be classified into urea condensation products, coated or encapsulated products, and supergranules (Trenkel, 1999).

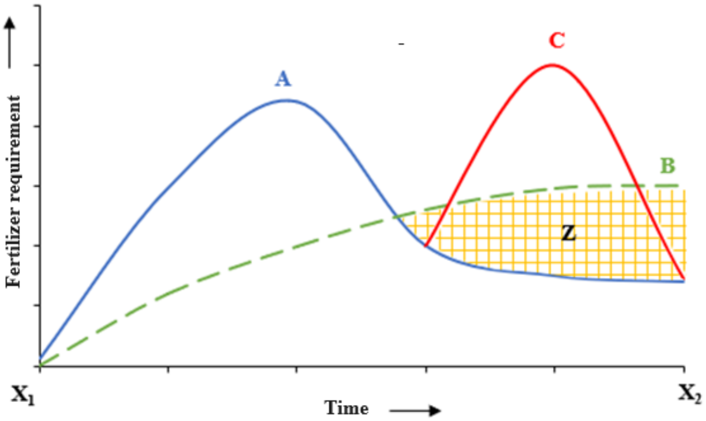

Figure 5. Fertilizer requirement in a crop, line A. Conventional fertilizer application, B. Actual crop requirement, C. Additional fertilizer application, Z. Difference between fertilizer applications and actual requirement. Adapted from Dave et al., 1999.

3.1.2. Urea condensation products

They are also known as low-solubility organic fertilizers and are compatible with most crops, depending on their use. They can be classified as urea-formaldehyde (UF), urea isobutyraldehyde (IBDU), and urea crotonaldehyde (CDU) (Shavit et al., 2002). The

UF are products that release the fertilizer through biological decomposition, remaining in the soil for 3 to 4 months, depending on the type of polymer, and contribute 38 % of nitrogen to the soil. While the IBDU and CDU products release the fertilizer through the gradual hydrolysis of the polymer through chemical decomposition, which transforms the urea from ammonium ions to nitrate, although its release process is influenced by temperature, humidity, and microorganisms, CDUs have a much larger particle size than IBDUs which makes the release more retarded (Trenkel, 1999).

3.1.3. Coated or encapsulated products

Encapsulation is a process by which the fertilizer is encased within a membrane, envelope, or polymer coating to control the interactions between the fertilizer and the outside (Risch, 1995; Borgogna et al., 2010). This cover can be made of hydrophobic materials such as polyolefins, polyurethane, polyethylene, alkyd resins, polyesters, or also hydrophilic materials such as gel or

hydrogels, in order to protect the active compound from the rapid degradation of the environment, modifying the physical characteristics of the fertilizer. Consequently, the stability of the original material is preserved to control the release of the fertilizer under the encapsulating matrix (Onwulata, 2012).

Recently, products with greater stability of the encapsulating material and better mechanical resistance have been developed (Chan et al., 2011). An example of these products is urea coated with sulfur, it is a product with a double coating, a primary one with sulfur and a second coating with a polymeric matrix. It degrades slowly through physical, chemical, or microbial processes, releasing sulfur as well as nitrogen, which is highly concentrated (30 – 40 %), reducing losses due to leaching or volatilization (Trenkel, 1999).

3.1.4. Supergranules

Supergranules are slow-release organic or inorganic compounds widely used in gardening and orchards, some special formulations contain urea formaldehyde, while others may be fertilizers such as ammonium metal phosphates or partially acidulated phosphate rocks (Trenkel, 1999). On the other hand, supergranules applications have a greater residual effect on the soil, Coutinho et al. (1991), report that these slow-release fertilizers can remain in the soil for up to two years after application, when used in semi-annual crops. Most slow-release fertilizers work with nitrogen encapsulation, in addition to this, super granules are also focused on the application and durability of other minerals such as potassium and phosphorus in the soil (Benites et al., 2013). These fertilizers are coated with polymers that are easily decomposed by chemical or microbial processes, minimizing losses by leaching the coated element and thus making it available for absorption by plants (Guarino et al., 2021).

4. Conclusions

Cassava is a crop of notable importance in the social-economic sphere as it is an important food in countries such as Colombia, but also a material of academic interest because of the properties of the starch derived from it and its potential for synthesizing materials.

The use of cassava starch in the production of biodegradable films can help reduce environmental pollution and the accumulation of non-degradable waste. Additionally, the abundance and low cost of cassava starch in many regions make it an economically viable option, making it an accessible raw material for industries seeking more sustainable solutions. Chemical or physical modifications can improve their properties and expand their applications in areas such as edible coatings, biodegradable packaging, protective films, and controlled release systems in agriculture.

In addition, the use of cassava starch-based biomaterials not only offers ecological benefits, but also creates opportunities for economic development, particularly in regions where cassava cultivation is prominent, the production and processing of starch-based biomaterials can generate employment and income, supporting local communities and contributing to their socioeconomic growth. However, more research and development are needed to fully unlock the potential of cassava starch in the production of innovative biomaterials, advances in processing technologies, functionalization methods, and compatibility with other materials will be crucial to optimize its performance. Due to this, continuous research plays a crucial role in the potential of cassava starch to foster a greener and more sustainable future in agro-industrial production.

Conflict interest. The authors declare that there is no conflict of interest.

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