UNIVERSIDAD DE INVESTIGACIÓN DE TECNOLOGÍA EXPERIMENTAL YACHAY

Escuela de Ciencias Químicas e Ingeniería

TÍTULO: A REVIEW OF THE APPLICATION OF POLYSACCHARIDES-BASED HYDROGELS AS CONTROLLED-RELEASE SYSTEMS OF FERTILIZERS

Trabajo de integración curricular presentado como requisito para la obtención del título de Química

Autor:

Natasha Anabelle Jurado Murillo

Tutor:

MSc. Lola María De Lima Eljuri

Tutor:

Ph.D Manuel Caetano Sousa

Urcuquí, enero 2022

Urcuquí, 21 de enero de 2022

SECRETARÍA GENERAL
(Vicerrectorado Académico/Cancillería)
ESCUELA DE CIENCIAS QUÍMICAS E INGENIERÍA
CARRERA DE QUÍMICA
ACTA DE DEFENSA No. UITEY-CHE-2022-00021-AD

A los 21 días del mes de enero de 2022, a las 09:00 horas, de manera virtual mediante videoconferencia, y ante el Tribunal Calificador, integrado por los docentes:

Presidente Tribunal de Defensa	Dr. SOMMER MARQUEZ, ALICIA ESTELA , Ph.D.
Miembro No Tutor	Dr. DIAZ BARRIOS, ANTONIO , Ph.D.
Tutor	Mgs. DE LIMA ELJURI, LOLA MARIA

El(la) señor(ita) estudiante **JURADO MURILLO, NATASHA ANABELLE**, con cédula de identidad No. **1751375278**, de la **ESCUELA DE CIENCIAS QUÍMICAS E INGENIERÍA**, de la Carrera de **QUÍMICA**, aprobada por el Consejo de Educación Superior (CES), mediante Resolución **RPC-SO-39-No.456-2014**, realiza a través de videoconferencia, la sustentación de su trabajo de titulación denominado: **A REVIEW OF THE APPLICATION OF POLYSACCHARIDES-BASED HYDROGELS AS CONTROLLED-RELEASE SYSTEMS OF FERTILIZERS**, previa a la obtención del título de **QUÍMICO/A**.

El citado trabajo de titulación, fue debidamente aprobado por el(los) docente(s):

Tutor	Mgs. DE LIMA ELJURI, LOLA MARIA

Y recibió las observaciones de los otros miembros del Tribunal Calificador, las mismas que han sido incorporadas por el(la) estudiante.

Previamente cumplidos los requisitos legales y reglamentarios, el trabajo de titulación fue sustentado por el(la) estudiante y examinado por los miembros del Tribunal Calificador. Escuchada la sustentación del trabajo de titulación a través de videoconferencia, que integró la exposición de el(la) estudiante sobre el contenido de la misma y las preguntas formuladas por los miembros del Tribunal, se califica la sustentación del trabajo de titulación con las siguientes calificaciones:

Tipo	Docente	Calificación
Miembro Tribunal De Defensa	Dr. DIAZ BARRIOS, ANTONIO , Ph.D.	10,0
Tutor	Mgs. DE LIMA ELJURI, LOLA MARIA	10,0
Presidente Tribunal De Defensa	Dr. SOMMER MARQUEZ, ALICIA ESTELA , Ph.D.	10,0

Lo que da un promedio de: **10 (Diez punto Cero)**, sobre 10 (diez), equivalente a: **APROBADO**

Para constancia de lo actuado, firman los miembros del Tribunal Calificador, el/la estudiante y el/la secretario ad-hoc.

Certifico que *en cumplimiento del Decreto Ejecutivo 1017 de 16 de marzo de 2020, la defensa de trabajo de titulación (o examen de grado modalidad teórico práctica) se realizó vía virtual, por lo que las firmas de los miembros del Tribunal de Defensa de Grado, constan en forma digital.*

JURADO MURILLO, NATASHA ANABELLE
Estudiante

NATASHA ANABELLE JURADO MURILLO
Firmado digitalmente por NATASHA ANABELLE JURADO MURILLO
Fecha: 2022.01.27 10:26:14 -05'00'

Dr. SOMMER MARQUEZ, ALICIA ESTELA , Ph.D.
Presidente Tribunal de Defensa

ALICIA ESTELA SOMMER MARQUEZ
Firmado digitalmente por ALICIA ESTELA SOMMER MARQUEZ
Fecha: 2022.01.25 09:48:32 -05'00'

Mgs. DE LIMA ELJURI, LOLA MARIA
Tutor

Firmado electrónicamente por:
LOLA MARIA DE LIMA

ANTONIO DIAZ BARRIOS

Firmado digitalmente por ANTONIO DIAZ BARRIOS
Fecha: 2022.01.21 23:30:45 -05'00'

Dr. DIAZ BARRIOS, ANTONIO , Ph.D.
Miembro No Tutor

Firmado electrónicamente por:
MARIELA SOLEDAD YEPEZ MERLO

YEPEZ MERLO, MARIELA SOLEDAD
Secretario Ad-hoc

AUTORÍA

Yo, **NATASHA ANABELLE JURADO MURILLO**, con cédula de identidad 1751375278, declaró que las ideas, juicios, valoraciones, interpretaciones, consultas bibliográficas, definiciones y conceptualizaciones expuestas en el presente trabajo; así cómo, los procedimientos y herramientas utilizadas en la investigación, son de absoluta responsabilidad de el/la autora (a) del trabajo de integración curricular. Así mismo, me acojo a los reglamentos internos de la Universidad de Investigación de Tecnología Experimental Yachay.

Urcuquí, enero 2022.

NATASHA ANABELLE JURADO MURILLO

Firmado digitalmente por NATASHA ANABELLE JURADO MURILLO
Fecha: 2022.01.27 10:27:39 -05'00'

Natasha Anabelle Jurado Murillo
CI:1751375278

AUTORIZACIÓN DE PUBLICACIÓN

Yo, **NATASHA ANABELLE JURADO MURILLO**, con cédula de identidad 1751375278, cedo a la Universidad de Investigación de Tecnología Experimental Yachay, los derechos de publicación de la presente obra, sin que deba haber un reconocimiento económico por este concepto. Declaro además que el texto del presente trabajo de titulación no podrá ser cedido a ninguna empresa editorial para su publicación u otros fines, sin contar previamente con la autorización escrita de la Universidad.

Asimismo, autorizo a la Universidad que realice la digitalización y publicación de este trabajo de integración curricular en el repositorio virtual, de conformidad a lo dispuesto en el Art. 144 de la Ley Orgánica de Educación Superior

Urcuquí, enero 2022.

NATASHA
ANABELLE
JURADO
MURILLO

Firmado digitalmente
por NATASHA ANABELLE
JURADO MURILLO
Fecha: 2022.01.27
10:28:36 -05'00'

Natasha Anabelle Jurado Murillo
CI:1751375278

DEDICATORIA

Este trabajo está dedicado a mi familia, los cuales han creído en mí siempre y me han apoyado incondicionalmente durante cada etapa de mi vida. Sin su amor y ayuda no hubiera sido posible alcanzar este logro. Ustedes son las personas que me inspiran a dar mi mayor esfuerzo y ser mejor cada día, los amo.

Natasha Anabelle Jurado Murillo

AGRADECIMIENTOS

En primer lugar, quiero dar gracias a DIOS por permitirme culminar mis estudios, y bendecir mi vida siempre.

A mis padres, Vinicio y Piedad por haberme dado todo su amor y apoyo durante toda mi vida, Dios no pudo haberme dado unos mejores padres, son mi orgullo y todo lo que he logrado y logre a futuro se los deberé a ustedes. Les agradezco por haberme educado con amor, por los sacrificios que han hecho para brindarme un buen futuro y por haber sembrado en mi valores y buenos sentimientos. Todas estas enseñanzas me han servido como herramienta a lo largo de mi vida y me han permitido convertirme en la persona que soy. Asimismo, quiero agradecer a mis hermanos Marco y Coralía quienes han sido mi apoyo y guía, y además de ser mis hermanos han sido mis mejores amigos y me han motivado e impulsado siempre. Agradezco a mi familia por haberme motivado constantemente, estoy orgullosa de todos ustedes y todos mis logros son y serán siempre para ustedes.

A mis tutores Lola De Lima y Manuel Caetano, por haberme guiado con paciencia y cariño durante todo el desarrollo de mi trabajo, les agradezco de corazón por el tiempo dedicado y la constante motivación. Considero que han sido unos excelentes tutores, que se caracterizan por su amplio conocimiento, experiencia y responsabilidad, pero sobre todo por su calidad humana.

Finalmente, quiero agradecer a todas las personas de mi entorno que me han apoyado, son personas maravillosas que han hecho de este viaje una experiencia más feliz, llena de buenos recuerdos y aprendizajes. Hemos crecido juntos y compartido una variedad de momentos increíbles. Gracias por brindarme su amistad, apoyo, e impulsarme a seguir luchando. Un agradecimiento especial a Omar por haberme brindado su cariño y apoyo siempre.

Natasha Anabelle Jurado Murillo

RESUMEN

Los hidrogeles son redes de polímeros con la capacidad de retener agua cuando se hinchan, lo que les permite proporcionar un medio interesante para la liberación controlada de fertilizantes. Aunque los avances más importantes en esta área se han logrado mediante el uso de polímeros sintéticos, actualmente existe una tendencia a incluir la fabricación de hidrogeles a partir de biopolímeros, para introducir biofuncionalidades específicas a los hidrogeles. Los biopolímeros son polímeros naturales que incluyen una amplia gama de polisacáridos (azúcares).

El siguiente trabajo se centra en los avances recientes en diseños de hidrogeles basados en polisacáridos, los diferentes enfoques de fabricación y sus aplicaciones. Se ha hecho énfasis especial en las modificaciones químicas que faciliten la liberación controlada y su relación con otras propiedades. La bibliografía fue seleccionada en base al contenido experimental relacionado con hidrogeles de polisacáridos eco-amigables, con liberación lenta de fertilizantes. Se utilizaron para ello diferentes bases de datos bibliográficas, incluyendo Scopus, SpringerLink y Google Scholar, cubriendo el período de 2015 a 2021.

Esta revisión tiene como objetivo brindar al lector una visión general actualizada de las propiedades de hidrogeles relacionadas con la liberación lenta, la capacidad de biodegradabilidad y las ventajas que ofrece este tipo de material en el campo agrícola, al mismo tiempo que muestra los beneficios de su aplicación en la conservación de suelos y medio ambiente, esperando incentivar su aplicación y mejorar la producción agrícola.

Palabras clave: Hidrogel; Polisacárido; Fertilizante; Liberación controlada; Biodegradable.

ABSTRACT

Hydrogels are networks of polymers with the ability to retain water when swollen, which allows them to provide an interesting media for controlled release fertilizers. Although the most important advances in this area have been achieved through the use of synthetic polymers, currently there is a trend to include the manufacture of hydrogels from biopolymers, to introduce specific biofunctionalities to hydrogels. Biopolymers are natural polymers that include a wide range of polysaccharides (e.g., sugars).

The following work is focused on recent progress in polysaccharide-based hydrogels designs, fabrication approaches and applications. Special emphasis on chemical modifications that facilitate controlled release and their relationship with other properties. The bibliography was selected based on the experimental content related to eco-friendly hydrogels with a slow release of fertilizers and polysaccharide-based, using different bibliographic databases, including Scopus, SpringerLink, and Google Scholar and covering the period from 2015 to 2021.

This review aims to provide the reader with a current overall view of hydrogels properties related to slow release, biodegradability capacity, and the advantages that offers this kind of material in the agricultural field, at the same time showing the benefits of its application in the soils and environment, to encourage its application and improve agricultural production.

Key words: Hydrogel; Polysaccharide; Fertilizer; Controlled release; Biodegradable

Table of Contents

LIST OF ABBREVIATIONS

(CTS) Chitosan
(CL) Cellulose
(ALG) Alginate
(GG) Gella Gum
(CG) Carrageenan
(GT) Gum Tragacanth
(St) Starch
(RHC) Rice husk chars
(CAN) Ceric Ammonium Nitrate
(APS) Ammonium Persulfate
(NR) Pre-vulcanized Natural Rubber
(PP) Polypropylene
(CMC) Carboxymethyl cellulose
(HEC) Hydroxyethyl cellulose
(GA) Glutaraldehyde
(SPA) Sodium polyacrylate
(PAA) Polyacrylic acid
(PVP) Polyvinyl pyrrolidone
(PLA) Poly (lactic acid)
(PVA) Poly (vinyl alcohol)
(CA) Citric acid
(Ur) Urea
($FeCl_3$) Iron (III) chloride hexahydrate
(KPS) Potassium persulfate
(IA) Itaconic acid
(S) Sulphur
(MKP) Monopotassium phosphate
(KNO_3) Potassium nitrate
(NPK) Nitrogen-Phosphate-Potassium

($CuSO_4$) Copper sulphate

(APP) Ammonium polyphosphate

(NPs) Nanoparticles

(NCNPs) Natural char nanoparticles

(AgNPs) Silver nanoparticles

($CaCO_3$) Biogenic calcium carbonate

(N-MBA) N, N’-methylene-bysacrylamide

(NaCMC) Sodium carboxymethyl cellulose

(CSAP) Commercial super absorbance polymer

(WSC) 1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide hydrochloride

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1: INTRODUCTION-JUSTIFICATION

The world population has grown over the years, and along with this, the demand for food. Because of this need, has been necessary the intensification of agriculture to satisfy the population demand[1]. According to the United Nations Food and Agriculture Organization (FAO), food production will have to increase by 70% to satisfy the demand for food in 2050, since it is projected that by that year the population will increase to 9.100 million inhabitants[2]. Along with this, an increase in the demand for agricultural products is expected, in the case of cereals is expected that by the year 2050 its about 3000 million tons is needed, to meet the population demand[2].

There is a growing concern that the current food supply system won't be able to expand at the rate needed to meet future demands. As a result, scientist have begun to search for new strategies to ensure we have enough food for the future[3]. The efficiency of agricultural production is primarily determined by the quality and quantity of nutrients that the crops receive. Fertilizers, agrochemicals composed mainly of nitrogen (N), phosphorus (P), and potassium (K), are the current sources of nutrients used in the agricultural industry[4]. A fertilizer will: keep the soil healthy, increase the number of crops yield, and determine crop quality and taste[5].

However, the mindless application of fertilizers for extended periods of time during intensive cropping negatively impacts the environment[1,5]. Conventional fertilizers are highly inefficient, their active compounds are released into the soil on application and will leech or evaporate faster than the crops can absorb them[1,5,6]. The loss of fertilizer produces a disbalance of nutrients in the soil, which results on farmers applying fertilizers several more times. The continuous application of fertilizers causes soil deterioration and acidification which declines their fertility. Also, the accumulation of nutrients that leech from the crops end up polluting the water of the surrounding rivers or lakes[5].

New fertilizer options have been developed to overcome this inefficiency, they release nutrients in a slow and controlled manner for a long period of time. These new options maintain a release speed such that the amount of nutrients available in the soils at any time match what the crops require for good development. Slow-release fertilizers reduce the environmental impact and the loss of fertilizers from leaching, volatilization, and degradation. Also, they improve the water holding in the soil and maintain the biological efficiency of active ingredients from fertilizer[1].

Controlled release fertilizers are present in different presentations as spheres, microspheres, nanoparticles, beads, hydrogels, and cyclodextrins[1]. Nowadays, the most popular system is a combination between hydrogels and fertilizers which together form a material of controlled release[7]. Hydrogels can be synthetic, natural, and semisynthetic. The hydrogels that are entering the agricultural field, are the natural-synthetic polymeric materials, which are formed by polysaccharides like cellulose, starch, dextran, chitosan, pectin, etc. They are characterized by their low cost, biodegradability, and availability[1]. These materials can also decrease the negative effects agriculture has on soils as erosion, compaction, and water loss.

Considering the importance of agricultural production for the world population, this work aims to show the impact of bio-friendly hydrogels on controlled release fertilizers; focusing on hydrogels generated from polysaccharides obtained from agricultural waste. This study seeks to raise awareness on the damage conventional fertilizers caused to the environment and provide an overview of controlled release hydrogels as an alternative option (which in addition to reducing the negative impact on the environment, can be produced from agricultural waste). These new materials can potentially help meet the future food demand while taking care of the environment.

1.1 PROBLEM STATEMENT

Agriculture is one of the main fields in a country since food production depends on it. However, due to its high demand, it has been necessary to work the soils excessively and use agrochemicals to improve the quantity and quality of the crops[1,3].The intensive cropping in the soils has caused the soils to wear out and lose their fertility, and for this reason, it has been necessary to use conventional fertilizers[5], which have generated a negative impact on the environment[8]. Since in some cases the concentration of nutrients in the soil is very high because of the immediately released from the fertilizer or in some other cases, the added nutrients are lost through volatilization, evaporation, and leaching, causing the lack of nutrients to the soils, in as much as the nutrients cannot be fully used, they can pollute the environment and at the same time, the waste of resources in an unnecessarily way since water and nutrients have to be constantly added to the soil, and then get lost[8]. This last, increase the cost of production of crops and at the same time the cost of the final product when it is on sale.

1.2 OBJECTIVES

1.2.1 General Objectives

The aim of this work is to show an overall view of polysaccharides-based hydrogels behavior for controlled release of nutrients, based on the main properties of hydrogels, and the relationship that they have with controlled release property, additionally show the factors that influence the hydrogel performance and know the generated advantages by the hydrogels used in the agricultural field.

1.2.2 Specific Objectives

- Know the impact of traditional fertilizers on the soil and environment.
- Learn the types, properties, and advantages of polysaccharides.
- Study the swelling, water-holding, water retention properties, which are related to polysaccharides-base hydrogels.
- Study the slow-release property from polysaccharides-based hydrogels, the advantages, and factors that could influence in its behavior.
- Study the biodegradability of hydrogels materials.

CHAPTER 2: THEORETICAL FOUNDATIONS

2.1 PLANTS AND SOIL

Quality of soils vary between fields, and even within the same field. These differences affect yield potential, therefore determining how watering and fertilization must be managed to reach acceptable production levels. There are some factors that can influence the concentration of nutrients in the soil, between the more important are the texture, pH, exchange capacity of cation, and anion[9].

- Texture

  The texture of soil will vary depending on the percentages of sand, silt, and clay in the composition of the soil, these components have an important role in the nutrition of the plants since of them will depend on the capacity to retain the water and nutrients in the soil[9,10]. Sand soil presents particles with a size smaller than 2 mm and larger than 0.05 mm, this kind of soil has a low capacity to retain water and nutrients, to its big pore spaces among particles and low surface area[9]. In the case of clay soil, it has particles smaller than 0.002 mm, which are able to hold big amounts of water and nutrients, since its small pores are able to avoid the draining of water, the soil has a high surface area that eases the absorption of the nutrients, due its fine clay texture and minerals with net charges in the surface[9]. Silt soil has a particle size between 0.05 to 0.002 mm been the middle point between the sand and clay soil which have large and small particles respectively[10].The soil can be composed completely of sand, clay, or silt however, this is not very common, since there are other types of soil formed by the combination of the three soils mentioned above, the other types of soils can be determined with the use of the soil texture triangle, which let know the percentage of composition of the other soils, the texture triangle is presented in **Figure 1**[9,10].

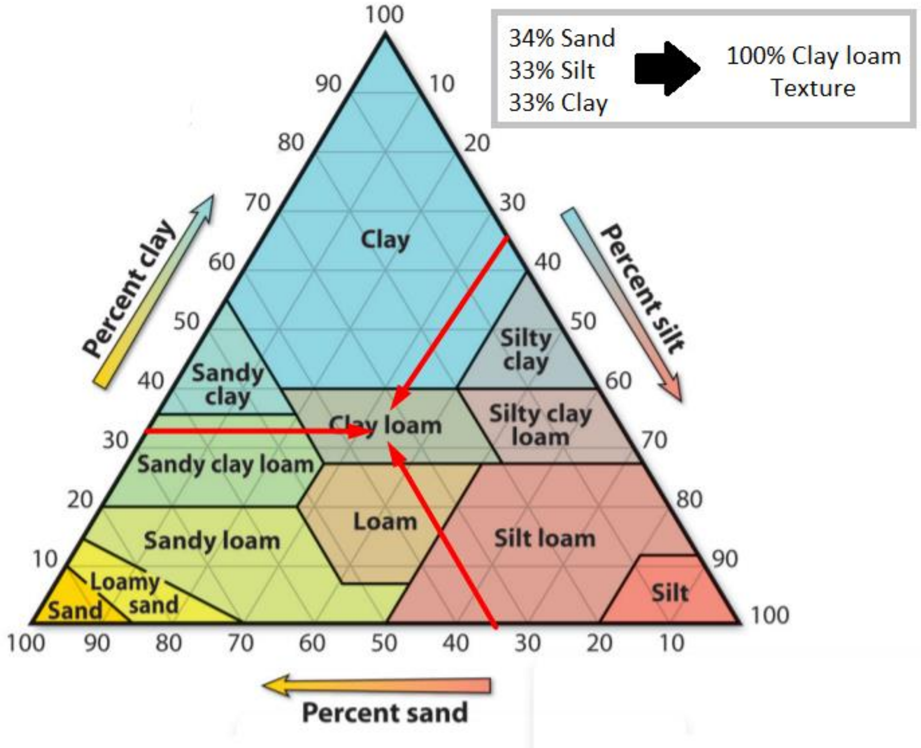

Figure 1. *Texture triangle (percentages of sand, silt and clay)*[10].

- pH

The soils present a certain pH, which let measure the hydrogen concentration (H^+), the acidic and alkaline soils present low and high pH levels respectively[9]. The pH value will depend on the nutrient availability, generally, the acidic soils present Cu, Fe, Mn, Ni and Zn, while the alkaline soils have a higher availability of base cations as Na^+, K^+, Ca^{+2} and Mg^{+2}[9]. The ideal pH is around 7, nevertheless is important to have in mind that nutritional necessities for each crop are different, in the same way, the pH value[9].

- Exchange capacity of cation, and anion

The particles of soil known as aluminosilicates or layer silicates can present negative charges attracted by cations, other types of soil have cations that attract anions[9]. The soils normally have a high amount of layer silicates hence, commonly present a net negative charge, which is recognized as cation exchange capacity (CEC)[9]. This term is used to express the ability of soil to hold and provide nutrients to the soil products. Additionally, the soils can retain anions, this capability is known as anion exchange capacity (AEC)[9]. Generally, CEC is higher than AEC, however, the AEC value is usually high enough to retain considerable amounts of any anion nutrients[9].

2.2 NUTRIENTS

One of the main factors that influence the quality and efficiency of the crops are the nutrients, the way in which they are applied to the soil will impact their performance[6].The essential nutrient is a term used to define a particular type of elements that are considered essential to achieve a favorable development in the plants, this term is related to certain criteria, they are fundamental nutrients for completing the lifecycle of the plants, these nutrients cannot be replaced by another element since they comply a specific function in the plant, also they are related to the metabolism of plants and for these reasons a high number of plants require of them to subsist[9,11]. There are 17 elements that are considered essential mineral elements for the correct development of plants[12,13]. The nutrients can be divided into two big groups which are the macronutrients and micronutrients, where the macronutrients are nutrients that plants need in higher amounts since the proper growth and development of crops depend on them, in addition, the micronutrients are necessary elements, but in smaller amounts in relation to macronutrients[12,14]. The distribution of macro and micronutrients is related to the necessities of the plant instead of the amount of nutrients absorbed by the plants[9]. From the essential elements, 9 are macronutrients C, H, O, N, K, Ca, Mg, P and S, they are present in the tissues of the plants at concentrations higher to 0.1% dry weight, in the case of micronutrients there are 8 essential elements which are B, Cl, Cu, Fe, Mn, Mo, Ni, and Zn, they are present at lower concentrations of 100 µg/g dry weight, the Cl and Ni elements are restricted micronutrients for certain types of plants and there are other elements that can be considered essential for a certain type of plants, they are grown in special environmental conditions[13]. C, H, O, N and S are the main elements of organic plants, they are constituents of amino acids, proteins, enzymes, and nucleic acids, the way in which the plants absorb these nutrients is related to oxidation-reduction reactions[11]. C, H, and O are non-mineral nutrients because they are obtained from air and water instead of soil minerals[9]. In the case of P, B, and Si, they are taken up from the soil as inorganic anions, acids and take place in plant cells or are linked by hydroxyl groups to compose esters of borate, phosphate and silicate[11]. Finally, the nutrients K, Na, Ca, Mg, Mn, and Cl are taken from the soil solution in the form of their ions, also from the plant cells where they are there in ionic form[11]. Micronutrients are fundamental nutrients that help to maintain the equilibrium of culture, the absence of any micronutrient could limit the growth of plants, even although the other nutrients are in the correct amount[12,14]. The concentration of the nutrients depends on certain factors as the type of plant, genotype, growth conditions, also of organs and tissues there are inside the plant, the interaction between these factors can influence the concentration of nutrients causing a lack or excess of them into the plants[13].

2.3 FERTILIZERS

The soils subjected to intensive cropping, present low amounts of nutrients and low efficiency, for that reason appears to the necessity to use fertilizers as a tool, with the objective to improve agricultural production and soil capacity[6]. The fertilizers are formed from a combination of nutrients, and once that they are dissolved they are instantly absorbed by the roots of the plants, the nutrients uptake will depend on the root capacity and nutrients concentration in the root outer[9]. The selective capacity of the plants to absorb the essential elements is limited, for that reason sometimes the plants take up unnecessary elements for their development that even could result toxic for them[11]. The plants take up the nutrients in their ionic or charged form since it is not possible in their elemental or no-charged form[9]. Each nutrient benefits in a different way to the plants, and its advantages vary depending on its functions. All the plants require a certain amount of nutrients, knowing them allows have an idea about the correct amount of nutrients required by the crop, and propose a fertilizer, that improves growth and production[9].

2.4 ENVIRONMENTAL PROBLEMS

Fertilizers are composed mainly of an active ingredient and other complementary reagents, to ensure an effective application[1]. The instantaneous release of fertilizer is the principal difficulty since produce a fast loss of chemicals, the loss of nutrients is related to the degradation process, and external factors as volatilization, evaporation, and leaching which occur once that fertilizers are added to the soil[1]. The concentration of nutrients is affected since that is consumed rapidly and as consequence, the crops receive a number of nutrients below the required amount to maintain their effectiveness[1]. Thus to ensure the appropriate dose is necessary spend more resources and apply the fertilizers repeatedly, causing environmental and health problems[1,6]. The excessive fertilization and neglected application have generated the salinity of the soil, accumulation of heavy metal, the eutrophication of water, and the accumulation of nitrates, which imply the air contamination by the generated gasses which contain nitrogen and sulfur, specially $NaNO_3$, NH_4NO_3, KCI, K_2SO_4, NH_4Cl that contributes to greenhouse effect[6]. The negative effects from fertilizers application are the contamination and degradation of soils, which cause an imbalance of nutrients in the soil, and an accumulation of toxic substances in the crops that can affect the health of the population[6]. By the negative impact of intensive application of fertilizers is complicated to obtain crops of quality[1,6]. The use of new materials as hydrogels like vehicles to transport nutrients and provide a slower release of nutrients has shown a reduction of toxic emissions, which means that is possible to reduce the negative impact caused by the fertilizers if are used other methods more ecofriendly[15].

2.5 POLYSACCHARIDES

Polysaccharides are macromolecules that are formed by monosaccharides, these molecules are linked by glycosidic bonds, and they are considered a relevant biological kind of polymer since are able to keep energy for many organisms[1,16]. They can be found easily in nature as plants resource (pectin, cellulose, starch, pectin, guar gum, and cyclodextrin), algae resource (alginate), microorganism resource(dextran, xanthan gum), and animal resource(chitosan, chondroitin)[1,17]. Polysaccharides can have a linear, branched or cyclic structure[16], and they can be classified as polyelectrolytes or non-polyelectrolytes, hence they can be charged positively, negatively, or can be neutral[1,17]. Their general formula is $C_x(H_2O)_y$ where x normally has a value around 200 to 2500[16]. These macromolecules are formed by a wide number of reactive groups, which present a large molecular weight, and differ in their chemical composition, which let an amply variety of options since each one is characterized by their structure and properties[17]. Their physical properties will be mostly determined by the shape of their molecules, and the shapes related to their chemical structure as the type of monomers, arrangements within the polymers chain, also internal connections, and ambiance[18]. The polysaccharides can be modified chemically or biochemically in an easy way, because of derivable groups presented in their structure, which let to obtain a diversity of polysaccharides derivatives[17]. Most of these macromolecules are conformed by hydrophilic groups (hydroxyl, amino, and carboxyl groups)[17]. Polysaccharides offer various advantages as a wide availability, low cost, high stability, safety, hydrophilicity, non-toxicity, biodegradability[1,17], which turn them an excellent option to be used for intensive production of materials or products based on them[1]. Currently, they are used in many fields as hygiene, biomedical, water treatment, electrical materials, buildings also in agriculture[8], which is one of the main applications of polysaccharides, since they are used to developed controlled release formulations that help to improve the crop production in an eco-friendly way[1].

2.5.1 Polysaccharides classification

Some of the more common polysaccharides used in agriculture field are presented:

- Cellulose (CL)

  Cellulose is a linear natural polymer known as the most abundant polysaccharide in nature, it is present in the cell wall of plants, algae, and bacteria, billions of cellulose is produced each year[1,8,16]. Cellulose molecule is a homopolymer, which is composed of a sequence of β-D-glucopyranose units which are linked by β-(1,4) glycosidic chemical bonds[1,19]. Cellulose properties will vary from polymerization degree and the length of the chain[16], its molecules are characterized by its biodegradability, low cost, biocompatibility with other polymers, and low toxicity, it is able to swell, and cannot dissolve in water. From its biodegradability property it can be degraded by many bacteria and fungi located in the air, soil, and water, and it can be transformed into CO_2 or water, which contributes to caring for the environment[1,19]. Cellulose commonly is used in pharmaceuticals, textiles, laminates, coatings, optical fields, and agriculture[19].

- Chitosan (CTS)

Chitin is widely available in nature and it is present on the exoskeleton of crustaceans, insects[19], also it can be found in the cell walls of some bacteria and fungi[1]. This substance is made up of D-glucosamine and N-acetyl-D-glucosamine monomers, which are linked by glycosidic bonds β-(1-4)[1,8,20]. Chitosan is a linear semicrystalline natural polymer formed by β-(1,4)-linked 2-deoxy-2-amino-D-glucopyranose units[8,19,20], it is obtained by the partial deacetylation of chitin in basic conditions[1]. The impurities amount, distribution of molar mass, and deacetylation degree of chitosan, it will depend on the natural resource used and the synthesis method[1]. This polysaccharide is the second more abundant in nature after cellulose and is widely used in many fields as biomedical, pharmaceutical, engineering, even agriculture since it presents many advantages as biocompatibility, biodegradability, and non-toxic characteristics[1,19,20], also it can be shaped in different forms like films, gels, membranes, etc. Additionally, it can be mixed with other polymers to form materials with good properties, given that it presents a cationic nature which let it ionic interactions with other compounds. It is sensitive to moisture and interacts well with water, for that reason must be combined with other compounds or reinforcing additives to improve its mechanical properties, if this is not made, the produced materials could present high permeability to water vapor[19].

- Starch (St)

It is a homopolysaccharide considered as one of the more abundant in nature, it is present in plants as cereal grains, legumes, roots, and fruits[1]. This molecule is a semi-crystalline polymer, which is composed of amylose and amylopectin chains, where amylose is conformed by units of glucose which are connected by α-(1,4) bonds in a linear chain, whereas amylopectin presents a branched structure among glucose through α-(1,4) and α-(1,6) bonds[1,8,19]. Amylase and amylopectin ratio are very important because improve the mechanical properties, this behavior is due to amylopectin which presents a linear structure, also by the water residue into starch which improves these properties while decreasing the glass transition temperature[19].

The starch molecule is characterized by its chemical stability, biocompatibility, low cost, and renewability. However, it presents some disadvantages as low mechanical strength, poor solubility by branched amylopectin which produces an accumulation, and high solubility at upper temperatures, which also present a weak barrier opposite to compounds with low polarity[19,20]. Another disadvantage is its brittleness which is related to its hydrophilic nature. Starch presents certain characteristics that can help to reduce pollution, taking into account its disadvantages previously explained, it is necessary to make modifications or mix it with other compounds to improve its properties[19,20].

- Carrageenan (CG)

It is an anionic polysaccharide that is sulfated, this polysaccharide is derived from red seaweed which is presented in many species of Rhodophyceae[18,19]. Carrageenan is water-soluble and present a lineal structure formed by alternating units of 1,3-linked β-D-galactopyranose and 1,4-linked α-D-galactopyranose, and presents a negative charge by the numerous ionized sulfate half-ester groups along the chain[18,19]. Carrageenan has three main isomers which can be distinguished based on their primary structure, they are iota-carrageenan, kappa-carrageenan, and lambda-carrageenan, which can be differenced by the number and positions of organosulfate groups in the repeating galactose units and disaccharide units[19,20]. The carrageenan presents good gelling properties due to its negative charge on each disaccharide and its characteristics are related to the sulfate ester group. This polysaccharide is widely used in many industries as food, packaging, pharmaceutical, and agriculture, since it presents some advantages as its low cost, biocompatibility, and easy use, without the necessity of chemical modifications[8,19].

- Alginate (ALG)

This is a linear polysaccharide that is obtained from the cell walls of brown macroalgae (Phaeophyceae)[1,8,19]. It is composed of two uronic acids 1-4 bond of β-D-mannuronic acid (M blocks) and α-L-guluronic acid (G blocks)[1,8,19]. Normally it is used as a tool for agrochemical release after passing through an ionotropic gelification process using metal ions[1]. This polysaccharide is characterized by its biocompatibility, high stability, unique colloidal properties, good gelling properties, immunogenic properties, non-toxicity, and it can be chemically and biochemically modified[8,19]. Alginate is used in many fields as food, packaging, pharmaceutical, biomedical, and agricultural. However, it presents some disadvantages as weak mechanical and water barrier properties, for this reason, must be modified or mixed with additives or synthetic polymers to improve its properties[19,20].

2.6 HYDROGELS FROM POLYSACCHARIDES

Hydrogels are three-dimensional structures that are crosslinked and are characterized by their hydrophilic behavior, which lets them absorb large amounts of water without being dissolved[1,21]. The retention ability is related to hydrophilic functional groups presented in their structure, which is linked to the backbone of the polymer, and the resistance to dissolution is due to cross-links between the chains in the matrix[21]. They are considered unique materials that have certain special characteristics like softness, water retention capacity, and are considered smart devices. From a macroscopic point of view, the hydrogel is formed by the union of several network chains which are connected with each other to form a macromolecule that is made by a liquid and a solid part, by its composition, the hydrogel has a relaxation behavior, hence the water into the network lets a free diffusion of solute molecules[21]. The elastic properties of the hydrogel are controlled by certain molecular characteristics, also its water volume after swell could change by different stimuli like temperature, solvent quality, pH, electric field and also by the media in which is applied[21,22]. The performance and structure of hydrogel will depend on the conditions in which was developed as the cross-linker concentration, dilution degree of monomers, also by the chemical units that make up the hydrogel structure, knowing these details lets understand their physical properties[21]. It can be formed from natural polysaccharides since as known, they present special features as their hydrophilicity and biodegradability properties. Polysaccharides have been used to controlled release formulations of fertilizers, given that are an eco-friendly option, which can help to reduce pollutions and health problems[1]. These formulations reduce the compaction, erosion, and run-off of soils and let also to improve the microbial activity, aeration, infiltration rates, and permeability, improve the quality of plants, and it also presents a safer way to apply agrochemicals. Currently, natural polymers have begun to replace synthetic polymers because of their low cost, widely availability, biodegradability, non-toxicity and ecological behavior[1]. The polysaccharide-based hydrogels are an excellent option as the raw material for hydrogels formulations by own to their properties and features[19]. As it was already mentioned before, polysaccharides can be easily found in nature and also they remain present in agro-industrial wastes which make them more accessible to be used[19]. As a reminder the more common polysaccharides there are cellulose, chitosan, starch, alginate, carrageenan, and many more that are available in the nature[19]. These hydrogels can be used in many industries as food, cosmetic, pharmaceutical, drug delivery, packaging, biomedical, hygiene and agriculture[8,19,23].

2.6.1 Types of hydrogels

Hydrogels can be developed from natural or synthetic polymers. Synthetic polymers are good mechanical properties, but their main problem is their low ability to be degraded, which causes a negative impact on the environment since require a long period of time to be degraded[1,22]. Whereas natural polymers present excellent biodegradability properties but they have weak mechanical properties which cannot be controlled, because of their composition, which restricts their use[1,22]. Polysaccharide hydrogels have shown potential in controlled release formulations, although by the disadvantages explained before, they must be chemically modified or mixed with additives or synthetic polymers to improve their mechanical properties and have better properties[8,23].

The terms hydrogels and the superabsorbent polymer (SAP), are related to the absorption and retention of large amounts of aqueous solutions[8]. Hydrogels are materials conformed by hydrophilic polymers that are crosslinked and form a three-dimensional network, they present a high ability to absorb water without being dissolved, when they are able to absorb more than twenty times of their weight base[23], they can be considered as superabsorbent hydrogels (SAHs)[8]. The SAPs are materials able to absorb high amounts of water since they can absorb thousand times their weight base, also they are conformed by ionic monomers, and by the lower crosslinking density they can absorb more water than the common hydrogels[8]. The SAHs are considered the best kind of hydrogel for business purpose since their volume represent around 80% of the hydrogel production[8]. The swelling capacity of the hydrogel can be affected by certain reasons, one of the most important is the ionic strength of the absorbed solution, which can decrease the swelling ability of hydrogel since the hydrogel will absorb a lower amount of solution in relation to being swelled with pure water[8]. The term superabsorbent is used to describe all the materials with the ability to absorb aqueous solutions, which includes hydrogels and

SAPs[8]. The more reported polysaccharide-based hydrogels in literature are cellulose, starch, chitosan, carrageenan, alginate, gella gum, arabic gum, linseed gum, gum tragacanth, and xanthan gum. Additionally, the derivatives from polysaccharides chemically modified more common are ethyl cellulose[24], carboxymethyl cellulose[25–28] and sodium carboxymethyl cellulose[12,14,29,30]. As was explained before, the polysaccharides hydrogels present many advantages as biodegradability, biocompatibility, non-toxicity, and are widely available in nature, however also present certain disadvantages as sensitivity to moisture and weak mechanical properties. These disadvantages can be improved by chemical modifications in polysaccharide structure (nature-modified hydrogel) or can be mixed with a synthetic polymer (semi-synthetic hydrogel), in some cases are added certain fillers (additives) as microcrystals, clay, $CaCO_3$ or nanoparticles ($AgNP_s$) which are going to improve the hydrogel performance[19].

2.6.2 Synthesis methods

Hydrogels can be obtained in different ways, the process includes the linking of the macromolecules chains together, which give as a result a three-dimensional network. The network structure present branched polymer initially, which after increase progressively its size and form a gel[23]. The most popular procedure is the synthetic process which normally is developed using free-radical, crosslinking, copolymerization or with the presence of hydrophilic non-ionic monomer which can be, acrylamide (AAm), or with a crosslinker as N,N’-Methylenebis (acrylamide) (MBAAm), which are commonly used to enhance the swelling capacity[21]. The crosslinking process can be developed through different techniques, which can be classified into physical or chemical crosslinking[22,23].

- Chemical crosslinking

  Hydrogels can be formed by chemical crosslinking giving as a result, hydrogels that present covalent joins. The swelling in the equilibrium state is dependent on crosslinking density, also on the kind of interactions between hydrogel and water[23]. Chemical crosslinking initiates with the polymerization of the functional groups that are available in the backbone, polymerization by the presence of the crosslinking agent, and crosslinking between polymers[23]. Polysaccharide hydrogels are performed through chemical crosslinking and can be obtained from diverse techniques. They can be synthesized with cross-linking agents, among the more common are formaldehyde, epichlorohydrin, MBAAm. The hydrogel formation through the chemical crosslinking method implies the cross-linking of active reaction sites as -OH groups which are available in the polysaccharide backbone[23]. The cross-linking process can be developed using a condensation reaction, Michael addition, hydrazone bonding, also enzymatic cross-linking. Another way to obtain the hydrogel using chemical cross-linking is through radiation, which does not require the chemical agents presence, this method develops biocompatible hydrogels which contribute to the environment. Radiation crosslinking is developed in one-step synthesis and is characterized by its accessibility, the cross-linking process is developed with high-energy radiations as gamma radiations, electron beam, or X-rays[23]. Crosslinking can be performed in dilute solution, concentrated solution, or in solid-state. Radiation-induced crosslinking is performed in aqueous state, and the irradiation of diluted solution give consequently the absorption of radiation by the water molecules, which will produce free radicals to activate the backbone of polysaccharide[23]. In addition when radiation-induced is performed in solid-state, free radicals are generated in the main polymer chain, and the primary reaction that occurs is the rupture of glycosidic bond, which therefore could cause the polysaccharide degradation, whose behavior will depend on reagents concentration and temperature[23]. Grafting copolymerization is one of the more used methods for hydrogel synthesis, which is related to covalent linkages of the monomer in the backbone of the polymer. The grafting copolymerization with a good chemical initiator or in presence of high radiations of energy is able to form macro-radicals which can be cross-linking and form a gel, also the chain of polysaccharide backbone could generate infinite branching and cross-linking[23]. Interpenetrating polymers networks (IPNs) are composed of two or more polymers, firstly one of the polymer networks is formed independently of the second polymer network which is formed immediately. IPN is developed in presence of a crosslinker and initiator. Currently, are widely used for their characteristics, since they are able to improve the mechanical properties and increase the phase stability of the product[22]. Chemical crosslinking is characterized to use initiator, crosslinker, free radical synthesis, and the product formation by radiation, also presents certain advantages such as high efficiency, easy availability to form molecules with high molecular weight, the irradiation is non-toxic and improves the mechanical strength of final products[22].

- Physical crosslinking

The crosslinking agents used normally are often toxic, for this reason is necessary to eliminate the residues before be used, however in physical crosslinking the hydrogel formation is developed without the presence of toxic reagents[22]. The hydrogels are formed when the networks are staying together, by the influence of secondary forces such as ionic interactions, hydrophobic interactions, or hydrogen bonding. The synthesis process of hydrogels is related to physical cross-linking where is not indispensable some cross-linking reagent presence, this is an efficient method to synthesized polymer networks[22]. Polysaccharides hydrogels can be developed with physical crosslinking, which can be achieved through many ways such as heating-cooling of polymer solution, ionic interactions, hydrogen bonding, heat-induced aggregation, coacervation complex, and freeze-drying[23]. Cooling of hot solution gives as a result the hydrogel formation, since the hot solution polymer is cooling, hence a helix is formed, which has certain junction zones in which present physical interactions. A stable gel is formed when the cooling is developed in presence of salts as K^+, Na^+, which improves the helix-promoting efficiency and will add more helices to form more stable gels[23,31]. Also, physical crosslinking can be developed as a reverse process, where the polymer solution is heated, and from the heating a copolymerization block is obtained[23]. The ionic interaction is achieved from the mixture of two polymers, one charged positively and the second charged negatively, and it is obtained by the addition of divalent or trivalent of counter ion polymer solution[23]. The hydrophobic interactions can form crosslinked hydrogels too. Also, the hydrogels with H-bonds can be developed at low pH, this process will imply a polymeric solution, which is crosslinked in the presence of an acid or polyfunctional monomer[23]. Freeze drying is an easy and efficient method to obtain the physically crosslinked hydrogels, this process is related to the microcrystals formation into the polymeric structure[23]. The self-assembling of polymer to form stereo complexes is a recent process, which is used to obtain physical-crosslinked hydrogels. This process consists of the use of enantiomeric lactic acid and methyl methacrylate oligomers to obtain the formation of stereocomplexes. The enantiomeric oligomers are joined to the polymer backbone for the hydrogel formation, these hydrogels are obtained by the mix of aqueous polymeric solutions[23]. Physical crosslinking is characterized by the formation of H-bond, ionic bonds, and electrostatic interaction, also presents certain advantages such as nontoxic behavior, it does not leave dissolvent residues, and sometimes does not require an initiator presence. However, present week mechanical strength[22].

Table 1. *General Information of polysaccharide-hydrogels*

Type and name of superabsorbent	Type	Polysaccharide	Derivative	Crosslinker/Initiator	Important additives	Composite preparation	Ref
Super water absorbing CHEDUR hydrogel	Natural-modified	Chitosan		EDTA-UREA (EDUR)		Crosslinking	[32]
Super absorbent hydrogel HAGG-CH	Natural-modified	Gellan gum Chitosan		Combination of CH and GG solutions		Crosslinking through ionic bond formation	[33]
*Urea-modified BA-Cell (CBA-Cell) hydrogel	Natural-modified	Cellulose		Urea		Crosslinking	[34]
Novel and eco-friendly chitosan/yeast hybrid hydrogels bead	Natural-modified	Chitosan			Yeast cell	Crosslinking by Alkali gelation	[35]
GEDTA hydrogel	Natural-modified	Cellulose	Cellulose acetate	EDTA		Esterification crosslinking	[36]
Linseed gum/cellulose superabsorbent hydrogels	Natural-modified	Cellulose Linseed gum		Epichlorohydrin		Crosslinking	[37]
Wheat straw based Semi-(IPNs) hydrogel Semi IPNs (WSC-g-PAA/PVA/NP) hydrogel	Semi-synthetic	Cellulose				Solution polymerization and graft copolymerization	[38]
Novel dual-layer slow-release nitrogen fertilizer (starch-SAP)	Semi-synthetic	Cellulose Starch From maize/ cassava/ potato	Ethyl cellulose	N-MBA/CAN		Crosslinking	[24]
High-swelling superabsorbent composite CMC-g-poly (AA-co-AMPS)/ATP	Semi-synthetic	Cellulose	CMC	N-MBA/APS		Grafting copolymerization	[25]
Super absorbent hydrogels ((CTS/Cell)-g-PAA-NPK) and ((CTS/Cell)-g-PAA)	Semi-synthetic	Chitosan-Cellulose		Thiourea formaldehyde		Chemical crosslinking and graft copolymerization	[39]
Superabsorbent nanocomposite SCMC-g-poly (AA)/PVP/Silica/NPK and SCMC-g-poly (AA)/PVP/Silica	Semi-synthetic	Cellulose Carboxymethyl cellulose From rice husk	CMC		Silica nanoparticles PVP	In-situ graft polymerization	[26]
Starch-based superabsorbent polymer (SBSAPs)	Semi-synthetic	Starch		N-MBA/CAN		Chemical crosslinking and graft copolymerization	[40]
Interpenetrating polymer networks (IPN NR/St) Hydrogel and (W-IPN-CUB) hydrogel	Natural-modified	Starch		Sulphur Glutaraldehyde	NR	Crosslinking-gelatinized	[15]
Superabsorbent hydrogel CHCAUR	Natural-modified	Chitosan			CA Urea	Hydrothermal synthesis and physical crosslinking	[41]
Poly (lactic acid)/cellulose based superabsorbent hydrogel	Natural-modified	Cellulose	NaCMC HEC	WSC	PLA	Crosslinking	[42]
	Natural-modified	Cellulose	CMC	Ca (2+) and K (+) ions	Sodium alginate	Ionic crosslinking	

Hydrogel k-carrageenan, sodium alginate and carboxymethyl cellulose based		k-carrageenan					[27]
K-carrageenan (k-CG) hydrogels	Natural-modified	k-carrageenan		Glutaraldehyde		Chemical crosslinking	[43]
k-carrageenan-based hydrogel (CBH)	Natural-modified	k-carrageenan			N-vinyl formamide Polyacrylamides	Co-polymerization process	[44]
NaCMC hydrogels CG hydrogels	Natural-modified	Cellulose Carrageenan	NaCMC	$FeCl_3$ Glutaraldehyde		Ionic crosslinking Chemical crosslinking	[14]
Lipase enzyme catalyzed biodegradable hydrogel-IPN system of GT with AAm and (MAA).	Semi-synthetic	Gum tragacanth				Crosslinking-grafting co-polymerization with lipase	[45]
Super absorbent hydrogel (SAH) of starch-modified poly (acrylic acid)	Semi-synthetic	Starch		N-MBA/APS		In situ polymerization-grafting	[46]
Hydrogel based on alginate-poly (vinyl alcohol)	Semi-synthetic	Alginate		Glutaraldehyde	PVA	Crosslinking-using solution mixing copolymerization method	[47]
PVC/CMC Superabsorbent hydrogels	Semi-synthetic	Cellulose	CMC		PVP	Gamma radiation-induced crosslinking	[28]
Chitosan-based (Qx-ox) superabsorbent hydrogels Chitosan-based (Qx-g-IA) superabsorbent hydrogels	Natural-modified	Chitosan				Oxidation under mild conditions Grafting copolymerization with IA	[48]
(NaCMC) hydrogels	Natural-modified	Cellulose	NaCMC	$FeCl_3$		Ionic crosslinking	[12]
Chitosan/polyacrylic acid /copper hydrogel nanocomposites (CS/PAA/Cu-HNCs)	Semi-synthetic	Chitosan			NPs	Ionic gelation and copolymerization	[49]
RHC/poly-(acrylic acid-co-acrylamide) (RHC/P) superabsorbents	Semi-synthetic	Cellulose From RHC		N-MBA/APS		Grafting copolymerization	[50]
Leftover rice-g-poly (acrylic acid)/montmorillonite/urea (LR-g-PAA/MMT/Urea) hydrogel	Semi-synthetic	From leftover rice		N-MBA/KPS		Grafting copolymerization	[51]
Biogenic calcium carbonate-reinforced PVA–alginate hydrogel $CaCO_3$-reinforced PVA-SA hydrogel	Semi-synthetic	Alginate			$CaCO_3$ PVA	Chemical crosslinking	[52]
Superabsorbents starches (SASs) from sweet cassava (NMUS), bitter cassava (NMES) and corn (CCS)	Natural-modified	Starch From corn/cassava and sweet cassava				Grafting copolymerization with IA	[53]
Urea encapsulated into salicylimine-chitosan hydrogels CS-Ux hydrogels	Natural-modified	Chitosan				In situ hydrogelation	[54]

AGBH and AGBCH hydrogels reinforced with eucalyptus and Pinus residues	Semi-synthetic	Arabic gum			Eucalyptus residues Pinus residues	Free-radical reaction	[55]
Coco peat-grafted-poly (acrylic acid)/NPK [CP-g-P(AAc)/NPK] hydrogel	Semi-synthetic	From Coco peat		N-MBA/NaOH		In situ polymerization-grafting	[56]
SC-g-PAA/PAM/Urea hydrogel	Semi-synthetic	From sawdust		N-MBA/KPS		Grafting copolymerization	[57]
Water-retaining, slow-release fertilizer (WSF) based in double-network hydrogels WSF hydrogel	Semi-synthetic	Cellulose	NaCMC		Urea-loaded halloysite	Ion-crosslinking and free radical polymerization	[29]
Super absorbent NaCMC-poly (AA-co-Aam hydrogel modified by rice husk	Semi-synthetic	Cellulose From rice husk ash	NaCMC	N-MBA/KPS	Silica nanoparticles	In situ polymerization-grafting	[30]
BPC-g-Poly (AA)/PVA)/LDH/NP hydrogel	Semi-synthetic	Cellulose From banana peel		N-MBA/APS	PVA	In situ graft polymerization	[58]
Starch-g-poly (acrylic acid-co-acrylamide) superabsorbent polymer with natural char nanoparticles (NCNPs) starch-g-poly (AA-co-AAm)/NCNps/Urea superabsorbent polymer	Semi-synthetic	Starch			NCNPs	In-situ polymerization	[59]
Cellulose-based hydrogel	Semi-synthetic	Cellulose From wheat straw		N-MBA/APS		Crosslinking-copolymerization	[60]
Novel semi-IPNs (MSP-g-AA/PVA-APP) hydrogel	Semi-synthetic	Cellulose				Graft polymerization and semi-IPNs	[61]
A series of carboxymethyl sago pulp (CMSP) hydrogels	Natura-modified	Hemicellulose Cellulose From sago pulp	Carboxymethyl sago pulp			Electron beam irradiation	[62]
Arabic gum-based hydrogel (MAGBH)	Semi-synthetic	Arabic gum				Co-polymerization	[63]
HCG and HCGP Super absorbent hydrogels (SAHs)	Semi-synthetic	Natural Cashew Tree		N-MBA/APS		Grafting-Crosslinking	[64]
A novel ecofriendly microwave-assisted xanthan gum-cl-poly (acrylic acid)/AgNPs (MW-XG-cl-pAA/AgNPs) hydrogel nanocomposite	Semi-synthetic	Xanthan gum		N-MBA/APS	AgNPs	Free radical graft polymerization	[65]
Hyd/RHA and Hyd/RHA/NPK superabsorbent nanocomposite	Semi-synthetic	Alginate From rice husk ash	Sodium Alginate	N-MBA/APS		In situ free-radical graft polymerization	[66]

CHAPTER 3: PROPERTIES OF HYDROGELS FROM POLYSACCHARIDES

3.1 SWELLING

Swelling is defined as a process in which the polymeric networks in presence of water show a volume change when they are exposed to external stimuli[67]. The swelling degree at equilibrium will depend on the cross-link and charge densities of the polymer networks[21]. The importance of evaluating the swelling is to know the maximum capacity of hydrogel to store water and nutrients. The swelling capacity of hydrogels can vary depending on some factors such as the type of crosslinker, ionic strength, and compositions of swelling solutions also they can be sensitive to environmental stimuli as temperature, pressure, light, salts, pH which can influence the swelling efficiency of hydrogels[8,67]. It is for this reason that studying how they affect the swelling of different hydrogel formulations is necessary to select the right hydrogel for a particular soil.

The main benefit gained from using hydrogels in agricultural soils is efficient resource management; the amount of water, fertilizer, and manpower needed to produce high-quality crops will be greatly reduced with the addition of hydrogels to the soil. One of the most important characteristics of hydrogels, that make this benefit possible, is swelling. Dry hydrogel with nutrients inside the matrix is added to the soil, then the soil is irrigated and the hydrogel swells with water. As the moisture of the soil decreases, the nutrients and water entrapped in the matrix are released gradually[7].

3.1.1 Swelling evaluation methodologies

The test consists of immersing the dry hydrogel in distilled water, deionized water, tap water, or any solution. The solvent penetrates the matrix and continues absorbing until reaches its equilibrium state, this behavior is the result of a diffusion process that is related to the molecules of solvent into the interior of the hydrogel 3D matrix[68,69]. In the equilibrium state, the elastic force repels the osmotic pressure and balances the stretching of the network to avoid deformations in the structure[68]. The ratio of the weight of the sample is known as the swelling ratio. To calculate the swelling ratio is used the equation(1)

$$Swelling\ ratio\ (Q_{eq}) = \frac{m_s - m_D}{m_s} \tag{1}$$

Where m_s represents the weight of swollen hydrogel sample per g and m_D the weight of dried hydrogel sample per g.

The equilibrium state occurs in the hydrogel when water molecules hydrate the hydrophilic group (primary water bond), and while the matrix continues to swell, the water molecules interact with other hydrophobic groups (secondary water bond). The combination of the two types of bonds creates the total water bond[68]. Also, the osmotic force is countered by the elastic retraction force, which produces the equilibrium state[68,69].

There are two main methods to evaluate the swelling in hydrogels. They are the beaker test method and tea bag test method. The most common of both is the beaker test.

- Beaker test

This test consists in introduce a hydrogel sample previously dried and weighted into a beaker, then the sample is immersed into a beaker that contains water, commonly distilled water. The sample continues absorbing water until achieving the equilibrium state. The swollen sample is removed from the beaker and the excess water is allowed to drop down for some minutes. Finally, the swollen sample is weighted, and its swelling ratio can be calculated using equation(1).

- Tea bag test

This test consists in introduce samples of hydrogel in different tea bags, the tea bags loaded with the hydrogel samples must be dried and weighed before being immersed into the beakers, then the different tea bags are immersed into a beaker that contains water, commonly distilled water. The sample continues absorbing water until achieving the equilibrium state. The swollen sample is removed from the beaker and the excess water is allowed to drop down for a minute. Finally, the swollen sample is weighted, and its swelling ratio can be calculated using equation(1).

3.1.2 Evaluated parameters

3.1.2.1 Hydrogel evaluation in water and salts solutions

The swelling on hydrogels occurs from the diffusion of water and inorganic or organic solutes into the hydrogel matrix through capillarity which is related to the physical interactions. The solutes and water molecules will be absorbed by the interactions generated from hydrophilic groups as carboxylates or amines, which are going to form hydrogen and covalent bonds. The swelling ratio is controlled by varying the crosslinking degree of the hydrogel network, chemical composition, temperature, pH, and the ionic forces of the solutions in which the hydrogel is evaluated[69].

The swelling ratio of hydrogels, absorption capacity, and the slow release of nutrients may be affected by the swelling solutions. The presences of ionic strengths create an unbalance between the osmotic pressure and the elasticity of the hydrogels while is swelling. The osmotic pressure appears as a consequence of the differences of ion concentrations that are inside and outside of the hydrogel matrix[69]. So, when decreasing the osmotic pressure, the swelling of hydrogel decreases too.

Mohammadi-Khoo et al.[34] prepared a hydrogel from modified cellulose and crosslinked it with urea. The hydrogel was evaluated in distilled water, tap water, and 0.9% NaCl and showed good swell behavior. From **Figure 2**, it is possible to observe that hydrogel has a higher swelling ratio in distilled water than in tap water and in 0.9% NaCl solution. Initially, the swelling is fast until reaches its maximum value. The swelling decrease in tap water is related to the presence of common ions present in tap water, which are responsible for water hardness. Finally, the lowest swelling was obtained in 0.9% NaCl, this reduction is related to the presence of ions of single valence. The results show a higher swelling behavior in distilled water > tap water > 0.9% NaCl[34].

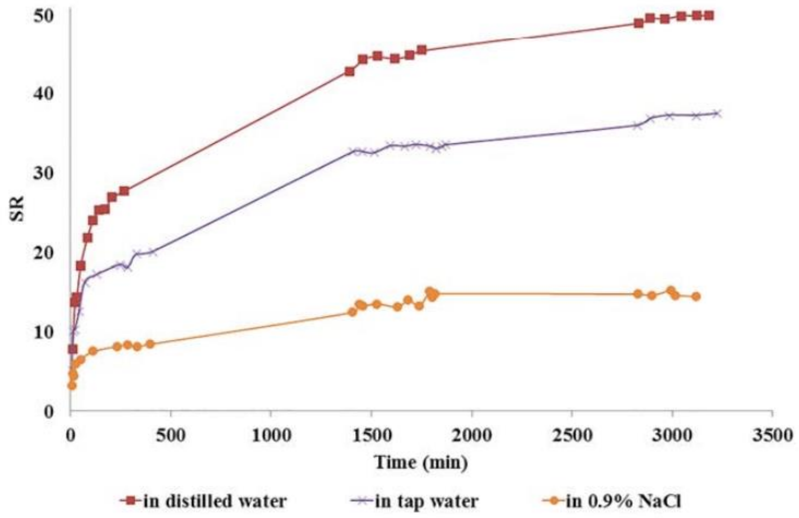

Figure 2. *Swelling behavior of CBA-Cell hydrogel in distilled water, tap water, and 0.9% NaCl solution*[34].

Souza et al.[55] prepared a composite hydrogel-based in Arabic gum, synthesized via free radical reaction. The hydrogel was evaluated in distilled water, drinking water, buffer solution at pH 7.0 and 4.0 the degree of swelling obtained was 20.21, 15.25, 10.95, and 9.83g/g. As shows the **Figure 3**, the distilled water had a higher swelling degree compared to the drinking water and buffer solutions. The decrease of swelling in drinking water is related to the mineral cations interactions with the glucuronic groups of the hydrogel that decrease the electrostatic repulsion forces. The swelling decrease of hydrogel in pH 7 is related to the attraction of electrostatic forces between cationic species from salts which are present in buffer solutions and polymer networks. Finally, the lower swelling degree was obtained in a buffer solution of pH 4, in which the gluconic groups are protonated at a pH lower than 7, so decreasing the swelling degree. Also, they were prepared Arabic-gum hydrogels reinforced with 5 and 10% of pinus residues and eucalyptus residues, these hydrogels were evaluated in the same way that Arabic gum hydrogels without reinforcement. The results show that the addition of residues increases the crosslinking density in the network of hydrogel and as consequence reduces the water absorption capacity. From the results is possible to say that swelling behavior is distilled water > drinking water > buffer solution at pH7 > buffer solution at pH 4[55].

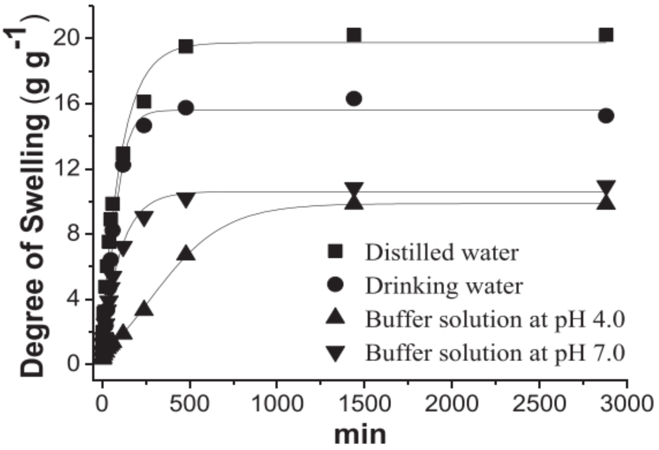

Figure 3. *Swelling behavior of Arabic gum-based hydrogel in distilled water, drinking water, buffer solution at pH 4.0 and 7.0*[55].

Pan et al.[50] prepared a series of rice husk char (RHC)/poly-(acrylic acid(AA)-co-Acrylamide(AM)) superabsorbent hydrogels, which were synthesized by graft copolymerization varying the amount of RHC. The hydrogels were evaluated in deionized water a) and in 0.9% NaCl solution b). The results were presented in **Figure 4**, in which the best swelling rate and swelling behavior were presented by the 1% RHC hydrogel. With a swelling ratio of 869g/g in deionized water and 97g/g in 0.9% NaCl solution. The evaluation in deionized water represented in **Figure 4(a)**, showed that in an amount < 1RHC the swelling behavior continues to be good, and it is better than the hydrogel without the presence of RHC. The presence of RHC in the polymer network improves the swelling capacity by the groups COO^- and C=O which lets that polymeric network have a better interaction with the water molecules, also, RHC presence improves and increases the porosity and the specific surface area of hydrogel facilitating the water penetration into the polymeric network. However, an excess of RHC in the polymer network as in the case of 2% and 5% RHC weakened the polymeric network decreasing the swelling capacity. The hydrogels evaluation in 0.9% NaCl solution presented in **Figure 4(b)**, shows a tendency similar to deionized water evaluation, however, it was notable the decrease of swelling ratio of hydrogels in 0.9% NaCl solution, this behavior is related to the charge screening effect which is produced by the counter ions of Na^+ present in the salt solution, that could weaken the electrostatic repulsion and decrease the osmotic pressure between the networks of hydrogel and the solution. From the results is possible to say that swelling behavior is distilled water > salt solution[50].

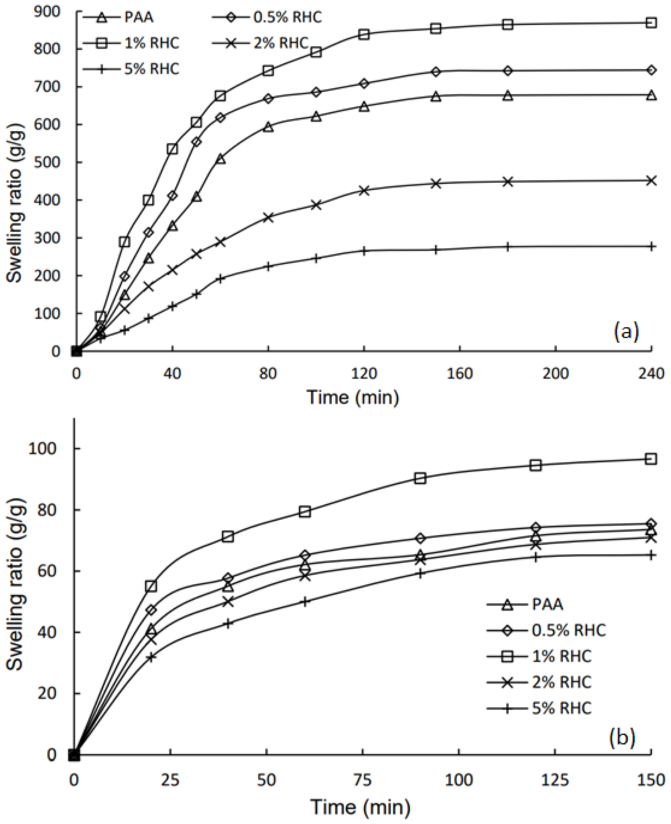

Figure 4. *(a) Swelling behavior of (RHC/P) superabsorbent hydrogel in deionized water*[50]*. (b) Swelling behavior of (RHC/P) superabsorbent hydrogel in 0.9% NaCl solution, where P is refers to PAA*[50]*.*

Feng et al.[35] prepared a chitosan/yeast hybrid hydrogel bead by introducing yeast cells into chitosan matrix through alkali gelation, the hydrogels were synthesized varying the percentage wt% of yeast from 0 to 50 wt% yeast. The swelling of hydrogels was evaluated in different salt solutions in KCl, NaCl, $MgCl_2$, $CaCl_2$, and $AlCl_3$ at a concentration of (0.1mmol/L). The results presented in **Figure 5**, show that hydrogel with a higher percentage of yeast (50 wt %) had the best performance in salt solutions. Showing a higher swelling in KCl > NaCl > $MgCl_2$ > $CaCl_2$ > $AlCl_3$. From the comparison of swelling in distilled water and salt solutions as was shown in the above studies, the performance in distilled water is better than in salt solutions. The swelling behavior of hydrogels in salt solutions decreases by the presence of multivalent metal cations which can form complexes with the hydrogen groups that are present in the chitosan/yeast hydrogel which increase the crosslinking density and ionic strength of salts solutions and as a consequence decrease the swelling capacity of the hydrogel[35]. When are compared two monovalent metal cations as K^+ and Na^+ or two polyvalent monoatomic cations as Mg^{2+} and Ca^{2+} present in the salt solutions in which hydrogel is evaluated, the solution with the cation of smaller radius size, will be let to hydrogel absorb a higher amount of solution[35].

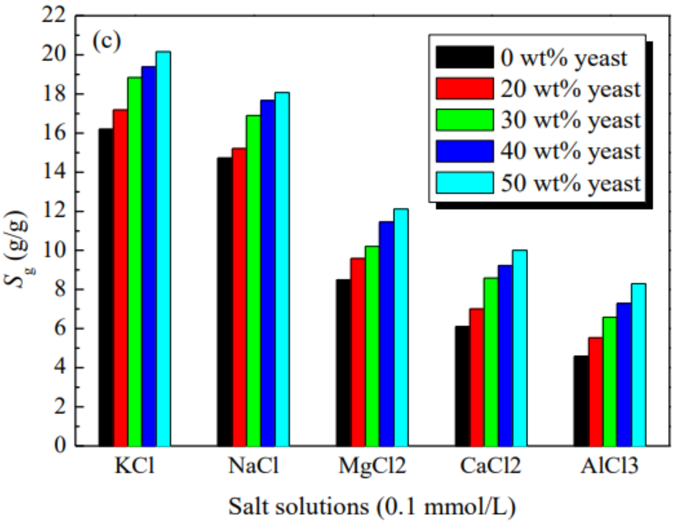

Figure 5. *Swelling behavior of chitosan/yeast hybrid hydrogel beads in different salt solutions (0.1 mmol/L)*[35].

X. Li et al.[38] prepared a wheat straw cellulose-g-poly(acrylic acid) (WSC-g-PAA) network and linear poly(vinyl alcohol) (PVA) was prepared using the method of solution polymerization. The hydrogel was evaluated in four different saline solutions NaCl, KCl, Na_2SO_4, and $CaCl_2$ at a concentration of (10mmol/L). From the results presented in **Figure 6**, it was possible to say that the presence of additional ions from salt solutions decreases the swelling rate and swelling capacity[38]. The same behavior was presented in the hydrogel performed by Feng et al.[35] this behavior occurs because the hydrogel had a higher swelling capacity in distilled water than in salt solutions which is a common phenomenon in the static swelling experiments of ionic hydrogels[38]. The performance of hydrogel in salts solutions decrease by the charge screening effect, which was caused by the presence of additional cations, for that reason, the charge screening effect gives as a result of a non-perfect electrostatic repulsion among anions, also the osmotic pressure between the internal network and external solution decrease because of ions presence. The swelling capacity in salt solutions increase in this way NaCl > KCl > Na_2SO_4 > $CaCl_2$[38].

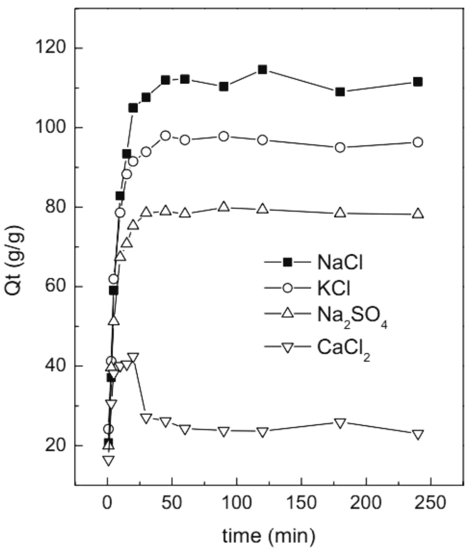

Figure 6. *Swelling behavior of WSC-g-PAA/PVA/NP hydrogel in different salt solutions (10mmol/L)*[38].

Zhou et al.[51] prepared a hydrogel using leftover rice-g-poly (acrylic acid)/montmorillonite which has incorporated urea in the network, the hydrogel (LR-g-PAA/MMT/Urea) was prepared through a crosslinking method. The hydrogel was evaluated in different salt solutions NaCl, $CaCl_2$, and $AlCl_3$ at a concentration of (0.10 mol/L). From the results present in **Figure 7**, it was possible to say that hydrogel has a higher swelling in distilled water than in salt solutions. The swelling performance in salt solution decrease in this way NaCl > $CaCl_2$ > $AlCl_3$. The swelling capacity decrease with the increasing of cationic charge and salt solution concentration, also the polyvalent cations as Ca^{2+} and Al^{3+} form intramolecular and intermolecular complexes with -COO- groups which let the formation of ionic crosslinking and increase the crosslinking density causing a decrease in the swelling and absorption capacity[51]. The swelling is inversely proportional to crosslinking density, also to the elastic modulus, which means that an increase in the crosslinker concentration, allows a higher crosslinking density and consequently will decrease the swelling capacity and increase the resistance of gel[8]. Since there is a diminishing in the space among the chains of the hydrogel network, hence decreases the elasticity of the polymeric network, hindering the penetration of water molecules to the hydrogel structure and as a result, the superabsorbent is more stable and compact[8].

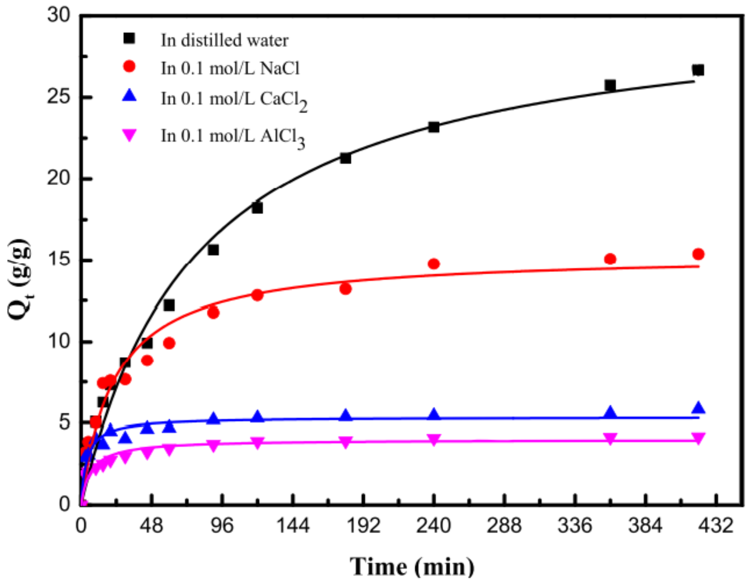

Figure 7. *Swelling behavior of LR-g-PAA/MMT/Urea hydrogel in distilled water and different salt solutions (0.10 mol/L)*[51].

Zhang et al.[57] prepared a hydrogel based on sawdust using grafting polymerization, nitrogen was incorporated from urea into the hydrogel. The hydrogel SC-g-PAA/PAM/Urea was evaluated in different saline solutions NaCl, $CaCl_2$, KCl, $MgCl_2$, and NH_4 at a concentration (10 mmol/L). From the results of **Figure 8**, it was concluded that hydrogel had a higher swelling in NaCl solution and a lower swelling in $CaCl_2$ solution. This behavior is explained by the cationic charge because while higher is the cationic charge, lower is the swelling of hydrogel. The water absorbency of the hydrogel in salt solutions follows the next order $Na^+ > K^+ > NH_4^+ > Mg^{2+} > Ca^{2+}$ and was argued by complex formation with the $-COO^-$ groups with multivalent cations, which can increase the crosslinking density of the matrix of the hydrogel. Also, the multivalent cations have a higher ionic strength than monovalent cations, for this reason, the water absorbency is lower in the salt solutions of multivalent cations, and in cations with the same charge, it is important to take into account the radius size, the smaller it is, the higher is the water absorbency of hydrogel[57].

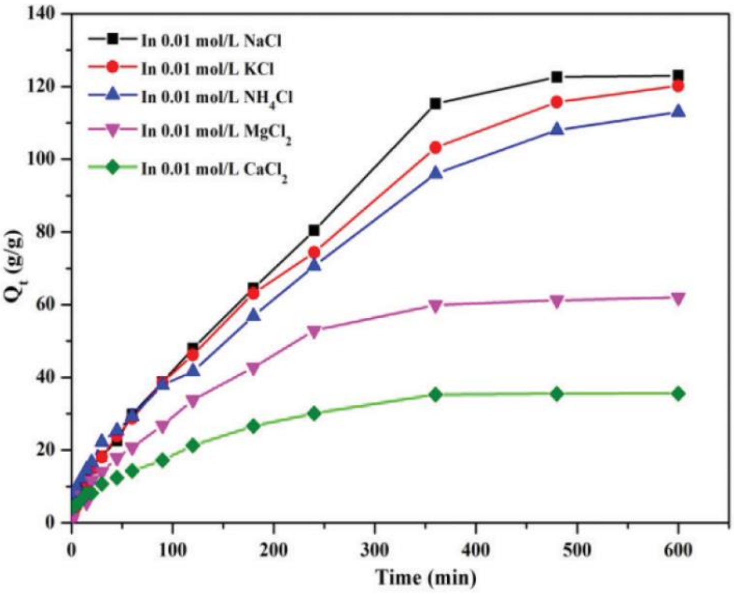

Figure 8. *Swelling behavior of SC-g-PAA/PAM/Urea in different salt solutions (0.01mol/L)*[57].

Olad et al.[66] prepared a hydrogel from sodium alginate, acrylic acid, acrylamide, and rice husk ash NaAlg-g-poly(AA-co-AAm)/RHA (Hyd/RHA) superabsorbent nanocomposite hydrogel, using the method of in situ free-radical graft copolymerization. The swelling of hydrogel was evaluated in different salt solutions NaCl, $CaCl_2$, $FeCl_3$ varying their concentrations from (0.1 to 1.1 wt%). The results presented in **Figure 9(a)**, showed a higher swelling in NaCl solution at lower concentration (0.1 wt%). This effect was related to the charge screening effect of cations in salt solutions, the cations protect the carboxylate anions and detain the electrostatic repulsion, and as consequence, the network is contracted and the swelling capacity decrease, because it increases the protection of the carboxylate anions, decreasing more the anion-anion repulsions between the carboxyl groups. In addition, the osmotic pressure difference between the internal part of the hydrogel matrix and the saline solution decreases in salt solutions with higher concentration, which is seen reflected in the decrease in the swelling of the hydrogel[66].

Zhang et al.[57] who prepared the SC-g-PAA/PAM/Urea hydrogel evaluated the swelling of its hydrogel in NaCl solutions at different concentrations (0.01 to 0.50mol/L). The results presented in **Figure 9(b)**, showed a higher swelling of the hydrogel at a low concentration of NaCl solution than a higher concentration. The results were explained by the inversely proportional behavior that there is between concentration and salt solution, which is related to the reduction of osmotic pressure difference, which works as a conductor force of swelling in hydrogel although by the increase of concentration in the salt solution, decrease the swelling capacity[57].

León et al.[48] prepared different hydrogels based on chitosan using two methods, oxidation under mild conditions and grafting of itaconic acid. The swelling behavior of oxidized and grafted chitosan in water hydrogels was evaluated in NaCl solution at different concentrations (0.009 to 0.9% w/v). From the results presented in **Figure 9(c)**, it is possible to say that Q2-g-IA hydrogel had the best performance in NaCl solution. It is observed that hydrogel has a better swelling in salt solution at low concentrations (0.009% w/v), and while increasing the concentration of NaCl solution decreases the swelling. This behavior is related to the ionic strength on the water absorbency in which the increment of ionic forces, decreases the swelling equilibrium by the increase of ionic concentration which preserves the negative charge of carboxylic acid groups present in chitosan[48].

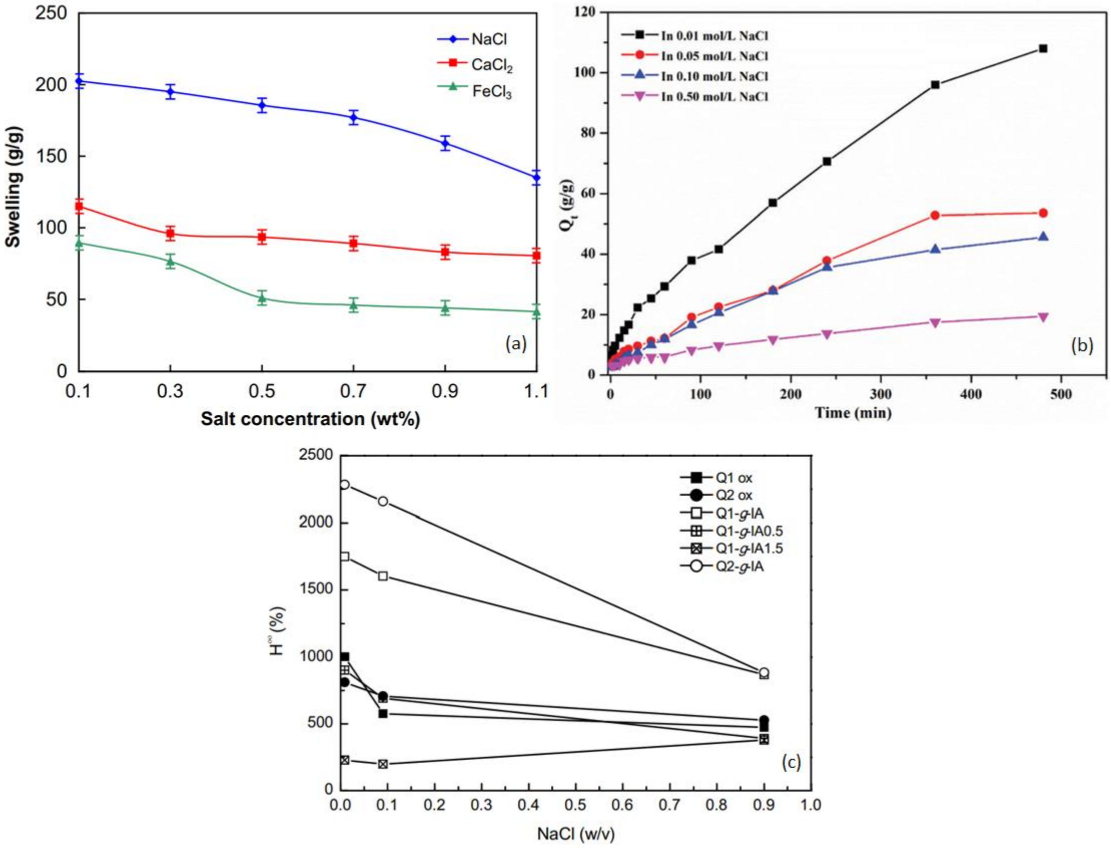

Figure 9. *(a) Swelling behavior of Hyd/RHA hydrogel in different salt solutions NaCl, $CaCl_2$, $FeCl_3$ at different concentrations (0.1 to 1.1 wt%)[66]. (b) Swelling behavior of SC-g-PAA/PAM/Urea hydrogel in NaCl solutions at different concentrations (0.01 to 0.50mol/L)[57]. (c) Swelling behavior of chitosan hydrogels in NaCl solutions at different concentrations (0.009 to 0.9% w/v)[48].*

3.1.2.2 Influence of pH in the swelling capacity

When the hydrogel is in an acid medium, the hydrogel matrix could be destabilized because the protonation of the anionic groups present in the matrix will increase. While the concentration of the anionic groups will tend to decrease[69]. This implies a decrease of electrostatic repulsion between the anions of the same or different chains. Therefore, at lower pH values the equilibrium state will be achieved in lower diffusion time[69]. The pH has high importance in the swelling capacity of hydrogel and the high or low swelling will depend on the groups present in the structure of hydrogel.

León et al.[48] evaluated the swelling capacity of its grafted and oxidized chitosan hydrogels in buffer solutions at different pH values. The results presented in **Figure 10(a)**, showed a higher swelling of all the samples at an acidic medium at pH 2. The grafted hydrogels had the higher swelling and Q2-g-IA hydrogel had the best swelling of all the samples. This behavior is related to the pKa because, at pH values higher than pKa the hydrogel does not let the solution go into the matrix so, the hydrogen bonds between carboxyl groups are interrupted also the $-NH_3^+$ ions give their charge to -COO- groups which produce a repulsion and as a consequence the swelling decrease. After to, pKa values of chitosan, its carboxylic groups (pKa value around 4) are in carboxylate form and for that reason it is caused a complete repulsion of water by the hydrogel. On the other hand, at pH values lower than pKa the water can penetrate the matrix, when the pH is very low the charge density of the matrix increases and many forces of electrostatic repulsion between $-NH_3^+$ are produced so, the hydrogel swells up. The groups involved in swelling equilibrium at different pH values are: $-NH_3^+$ and -COOH at pH=1 to 3, $-NH_2$ and -COOH or $-NH_3^+$ and $-COO^-$ at pH= 4 to 7, and $-NH_2$ and $-COO^-$ at pH= 7 to 13[48].

Pan et al.[50] evaluated the swelling of their hydrogels RHC/P with different percentages of RHC in different pHs, using 1mol/L NaOH or HCl solution. The results presented in **Figure 10(b)**, showed a higher swelling for all the samples at pH between 6 to 8. The highest swelling was obtained by the hydrogel with 1% RHC/P. In the samples with a value percentage higher than 1% of RHC, the swelling was poorly visible, while in samples with a percentage of RHC lower than 1% had the higher swelling behavior. The higher swelling was obtained at pH between 6 to 8 and is related to the buffer action of -COOH and -COO, where the buffer function disappears by the excess addition of acid or base. At pH lower to 4 the carboxylate groups are protonated so, the hydrogel bonding between carboxylates groups is fortified and was produced an additional physical crosslinking. Also, the electrostatic repulsion between carboxylate groups was limited and the matrix contracts and for this reason the swelling decrease. While at pH values higher than 8 it is possible to see a decrease in the swelling capacity, because at highly basic solutions the excess of Na^+ causes the charge screening effect, which protects carboxylate anions, and prevents the effective repulsion anion-anion[50].

Soliman et al.[25] prepared a superabsorbent composite CMC-g-poly (acrylic acid-2acrylamide2-methylpropane sulfonic acid)/Attapulgite based on carboxymethyl cellulose (CMC) and inorganic clay attapulgite (ATP) using the grafting copolymerization method. The swelling ability of hydrogel was evaluated in NaOH (pH 13) and HCl (pH 1.0) solutions to evaluate the behavior of hydrogel at different pH. The superabsorbent hydrogel containing different groups in the structure as carboxylate, carboxamide, and sulfonate groups is an anionic superabsorbent. From the results presented in **Figure 10(c)**, it is possible to observe the highest swelling behavior a pH values between 6 to 9, in this range the -COOH and $-SO_3H$ groups were converted in $-COO^-$ and SO_3^- and the interaction of hydrogen bonding was eliminated, so the electrostatic repulsion between the anionic groups increases in this pH values. At pH values lower to 6 the carboxylate and sulfonate groups of the hydrogel were converted into carboxylic acid and sulfonic acid groups. And finally at pH values higher than 9 (basic solution) the swelling behavior decrease by the charge screening effect from counterions (Na^+)[25].

Olad et al.[66] prepared a (Hyd/RHA) hydrogel using in situ free-radical graft copolymerization. The swelling of hydrogel was evaluated in dilute aqueous solutions of NaOH (0.1M) and HCl (0.1M). From the results presented in **Figure 10(d)**, it is possible to say that the best swelling behavior of hydrogel was obtained at a pH value of 6. At pH values lower to 5 (acidic medium) it is possible to see a decrease of swelling capacity which is related to the strong hydrogen-bonding interactions which let the formation of physical crosslinking points in the hydrogel, because of the decreasing of electrostatic repulsive forces between carboxylate anions, so the network is contracted and the swelling decrease. At pH values between 5 to 9 the dissociation degree of carboxylic groups is higher so, the electrostatic repulsive forces between carboxylate anions are higher and the swelling capacity is higher. Finally, at pH values higher than 9 (basic medium) the swelling behavior decrease because of the protector effect of Na^+ counterions in $-COO^-$ avoid the effective repulsions anion-anion, causing a contracted network which causes a decrease in the swelling of hydrogel[66].

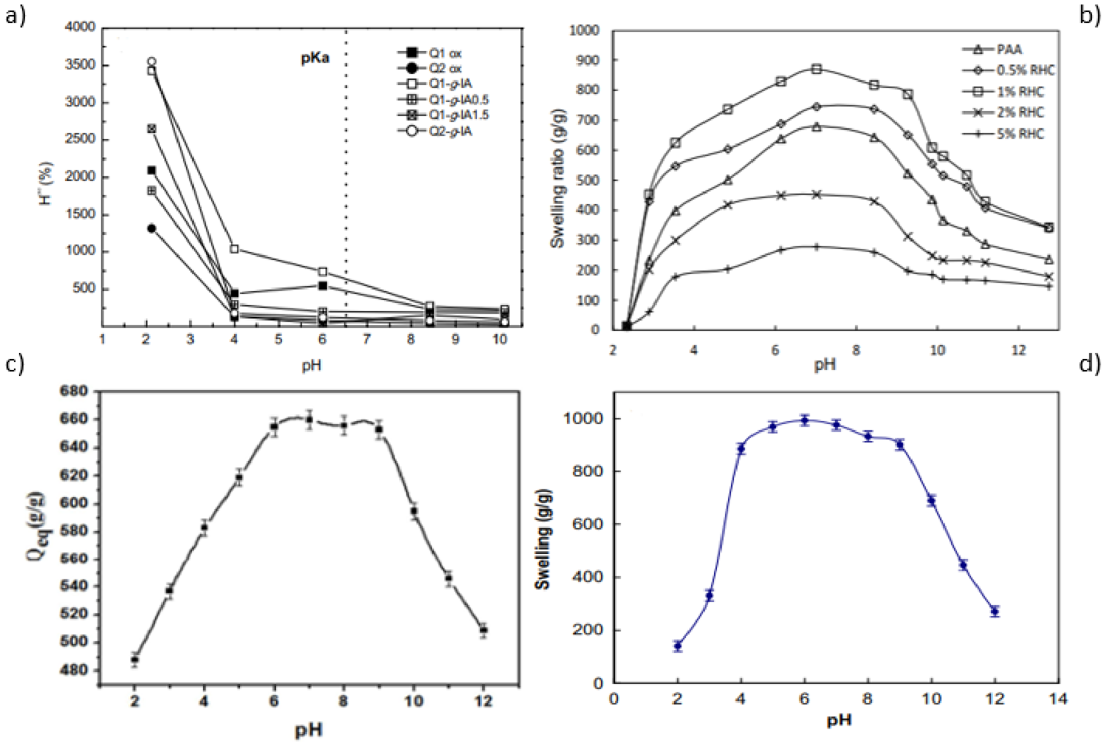

Figure 10. *(a) Swelling behavior of chitosan hydrogels at different pH values*[48]*. (b) Swelling behavior of RHC/P hydrogels at different pH values*[50]*. (c) Swelling behavior of CMC-g-poly(AA-co-AMPS)/ATP at different pH values*[25]*. (d) Swelling behavior of hyd/RHA hydrogel at different pH values*[66]*.*

__Table 2.__ Swelling behavior of hydrogels in different aqueous solutions

Type and name of superabsorbent	Maximum swelling (Qeq) in g/g or %				Kinetic mechanism	Ref
	Water	Salt solutions	Buffer solution			
			pH	Qeq		
Super water-absorbing CHEDUR hydrogel	570 DW-1	150 NaCl				[32]
Super absorbent hydrogel HAGG-CH	219 DW-1					[33]
*Urea-modified BA-Cell (CBA-Cell) hydrogel	49.80 DW-1 / 27.94 TW	11.04 NaCl	7	50	Non-Fickian diffusion	[34]
Novel and eco-friendly chitosan/yeast hybrid hydrogels bead	31.7 DW-1	20 KCl / 18.5 NaCl / 12 MgCl / 10 $CaCl_2$ / 8.6 $AlCl_3$	6	20.6	Pseudo second order kinetic model	[35]
GEDTA hydrogel	1000% DW-1		8.5	1000%		[36]
linseed gum/cellulose superabsorbent hydrogels	310 DW-1	215 NaCl / 225 $CaCl_2$				[37]
Wheat straw based Semi-(IPNs) hydrogel Semi- IPNs (WSC-g-PAA/PVA/NP) hydrogel	180 DW-1	123.73 NaCl / 40 $CaCl_2$ / 83.06 Na_2SO_4	7	180	Schott's second order	[38]
Novel dual-layer slow-release nitrogen fertilizer (starch-SAP)	137.1 DW-1				Pseudo-first order kinetic model	[24]
High-swelling superabsorbent composite CMC-g-poly (AA-co-AMPS)/ATP	864 DW-1	150 NaCl / 130 $MgCl_2$ / 53 $CaCl_2$ / 38 $AlCl_3$	7	660		[25]
Super absorbent hydrogels ((CTS/Cell)-g-PAA-NPK) and ((CTS/Cell)-g-PAA)	390 DW-1	39.5 NaCl				[39]
Superabsorbent nanocomposite SCMC-g-poly (AA)/PVP/Silica/NPK and SCMC-g-poly (AA)/PVP/Silica	770 DW-1	120 NaCl				[26]
Starch-based superabsorbent polymer (SBSAPs)	253.33 DW-1					[40]
Interpenetrating polymer networks (IPN NR/St) Hydrogel and (W-IPN-CUB) hydrogel	43.8% DW-1					[15]
Superabsorbent hydrogel CHCAUR	1250 DW-1	210 NaCl				[41]
Poly (lactic acid)/cellulose based superabsorbent hydrogel	300 DW-1					[42]

Hydrogel k-carrageenan, sodium alginate and carboxymethyl cellulose based	22.5DW-1					[27]
K-carrageenan (k-CG) hydrogels			12	18,83		[43]
K-carrageenan-based hydrogel (CBH)	80 DW-1					[44]
NaCMC hydrogels	400% DW-1					[14]
CG hydrogels	635% DW-1					
Lipase enzyme catalyzed biodegradable hydrogel-IPN system of GT with AAm and (MAA).	259.04% DW-1					[45]
Super absorbent hydrogel (SAH) of starch-modified poly (acrylic acid)	700 DW-1	61.94 NaCl / 2.67 $CaCl_2$				[46]
Hydrogel based on alginate-poly (vinyl alcohol)	430% DW-2					[47]
PVC/CMC Superabsorbent hydrogels	261 DW-1		6	70		[28]
Chitosan-based (Q1-ox) superabsorbent hydrogels	1050% DW-1 / 550% TW		2	2100%		[48]
Chitosan-based (Q2-g-IA) superabsorbent hydrogels	2300% DW-1 / 2200% TW			3500%		
Chitosan/polyacrylic acid /copper hydrogel nanocomposites (CS/PAA/Cu-HNCs)	185% DW-1					[49]
RHC/poly- (acrylic acid-co-acrylamide) (RHC/P) superabsorbents	869 DW-2	97 NaCl	7	869		[50]
Leftover rice-g-poly (acrylic acid)/montmorillonite/urea (LR-g-PAA/MMT/Urea) hydrogel	102.6 DW-1	15.34 NaCl / 5.33 $CaCl_2$ / 4.01 $AlCl_3$			Schott's pseudo-second-order	[51]
Biogenic calcium carbonate-reinforced PVA–alginate hydrogel CaCO3-reinforced PVA-SA hydrogel	160% DW-1					[52]
Superabsorbents starches (SASs)-CMUS (sweet cassava)	10 000% DW-1		8.5	7500%		[53]
Superabsorbents starches (SASs)-CMES (bitter cassava)	5550% DW-1		6	5250%		
Superabsorbents starches (SASs)-CCS (Corn)	1850% DW-1					
Urea encapsulated into salicylimine-chitosan hydrogels CS-Ux hydrogels	68 DW-1		6	68		[54]

AGBH and AGBCH hydrogels reinforced with eucalyptus and pinus residues	20.21 DW-1 / 15.25 PW		7	10.95	Fickian diffusion	[55]
Coco peat-grafted-poly (acrylic acid)/NPK [CP-g-P(AAc)/NPK] hydrogel	165 DW-1					[56]
SC-g-PAA/PAM/Urea hydrogel	210 DW-1	125.87 KCl / 131.25 NaCl / 71.79 $MgCl_2$ / 39.4 $CaCl_2$ / 114.94 NH_4Cl	7	225	Schott's second-order	[57]
water-retaining, slow-release fertilizer (WSF) based in double-network hydrogels WSF hydrogel	110.2 DW-1	33.1 NaCl / 29.9 $CaCl_2$ / 23 $FeCl_3$			Non-Fickian diffusion	[29]
Super absorbent NaCMC-poly (AA-co-Aam hydrogel modified by rice husk	650.10 DW-1					[30]
BPC-g-Poly (AA)/PVA)/LDH/NP hydrogel	233.61 DW-1	96.53 KCl / 110. 75 NaCl / 23 $CaCl_2$ / 76.02 Na_2SO_4			Schott's second-order	[58]
Starch-g-poly (AA-co-AAm)/NCNps/Urea superabsorbent polymer	334.3 DW-2					[59]
Cellulose-based hydrogel	3095.74% DW-1					[60]
Novel semi-IPNs (MSP-g-AA/PVA-APP) hydrogel	681.3 DW-2					[61]
Arabic gum-based hydrogel (MAGBH)	21 PW		7	9	Non-Fickian diffusion	[63]
HCG and HCGP Super absorbent hydrogels (SAHs)	240 DW-1		12	240		[64]
A novel ecofriendly microwave-assisted xanthan gum-cl-poly (acrylic acid)/AgNPs (MW-XG-cl-pAA/AgNPs) hydrogel nanocomposite	1910% DW-2	1000% KCl / 1100% NaCl / 850% $CaCl_2$ / 650% $FeCl_3$			Moves toward non-Fickian to Fickian	[65]
Hyd/RHA and Hyd/RHA/NPK superabsorbent nanocomposite	1070 DW-1	200 $NaCl_2$ / 120 $CaCl_2$ / 87 $FeCl_3$	6	993		[66]

Where DW-1 is distilled water, Dw-2 is deionized water, TW is tap water and PW is pure water

3.2 WATER-HOLDING CAPACITY AND WATER RETENTION CAPACITY OF SOILS AND HYDROGELS

Water holding capacity (WHC) and water retention capacity (WRC) are important properties related to the presence of water in the soil. Water holding capacity is described as the total amount of water that the soil can hold between the field capacity and withering point, while water retention capacity is related to the real water quantity retained for agricultural use[70]. There are many kinds of soils, each one has different characteristics and presents distinct pore sizes, which influence water retention[14]. The soils with large pore sizes restrict the water retention and accelerate the release of nutrients to the soil, whereas soils with small pores improve water retention and enable a slower release of nutrients[14]. The wear of soil and water holding increases the complexity of crop production and makes them more expensive, especially in sectors with low water accessibility[65]. Polymeric hydrogels have been used as an alternative to improve crop production, because they can absorb large amounts of water, and therefore, improve the water holding capacity of the soil and promote the growth of the plants in unfavorable conditions[14,51]. The hydrogel performance with regard to water holding and retentions is directly related to porosity and swelling behavior since the porous surfaces and swelling of hydrogel material will allow higher water retention[65]. Hydrogel have shown to be an alternative to improve the use of water, save resources, decrease the irrigation cycles, and improve the oxygenation of plants[66,69]. Since, when hydrogel is mixed with soil, the hydrogel samples increase their dimensions by the swelling, which increase the porosity of the soil and provide a better oxygenation in the roots of the plants[69,71].

3.2.1 Evaluation methods of WHC and WRC

In some experimental works, is evaluated the water holding capacity and water retention capacity of hydrogels, with the objective of knowing the efficiency of hydrogel formulations to hold water in the soil. There are many methods to study WHC and WRC. In the case of water holding, capacity in the literature can be found as water holding[34,46,57,59,72] or the largest water-holding ratio (WH%)[54]. Whereas in the case of water retention capacity in the literature can be found as water retention[25,26,38,42,43,58–60,66], water-retention ratio[34,37,47], water evaporation ratio[33,36,39,51,56,65], moisture retention[27,41], moisture gain[45], moisture content, or water-retaining ratio (WR%)[29].

WHC and WRC of hydrogels can be studied in the soil, or directly analyzing the swollen sample.

3.2.1.1 General evaluation methods of water-holding (WH%)

The methodologies to evaluate the WHC have the same principles, however, some steps within the procedure can vary.

Firstly, two samples of soil must be collected. One will be weighted with the hydrogel sample and the other becomes the control sample (to compare the behavior of soil without the presence of hydrogel). The treated soils (with hydrogels) and untreated soil (control) are placed into a container[27] that could be a plastic pipe (1cm)[34], polyvinyl chloride tube (4.5cm)[57], or PP columns[59] sealed in the bottom with nylon mesh or filter paper, or another option is to use a beaker with small holes at the bottom[46]. Subsequently, the water (distilled, deionized, or tap water) is added slowly from the top until the water seeps out from the bottom of the container, the container is weighed again when seepage has stopped. In some cases, a specific amount of water is added to the samples and the samples are again weighted after a certain time.

The increase in the water-holding capacity of soil WH % can be calculated using the next equations(2)(3)(4).

$$WH\ \% = \frac{(W_2 - W_1)}{W_0} \times 100 \tag{2}$$

$$WH\ \% = \frac{(W_2 - W_1)}{W_1} \times 100 \tag{3}$$

$$WH\ \% = \frac{(W_2 - W_1)}{W_2} \times 100 \tag{4}$$

Where: W_0 represents the weight of container having pure soil, W_1 is the weight of the container with soil + hydrogel sample dry, and W_2 is the weight of the container with soil + hydrogel after seepage was stopped.

Note: The amounts of soil, hydrogel, and water will vary depending on the people conducting the test.

3.2.1.2 General evaluation methods of water-retention (WR %)

Water retention methodologies can be evaluated with hydrogels in the soil or just the swollen hydrogel sample.

3.2.1.2.1 Water-retention of swollen hydrogel samples

The study of water retention of hydrogel without soil presence is done by analyzing the water evaporation kinetics of a previously swollen hydrogel until equilibrium with water (distilled, deionized, or tap water)[33]. The swollen samples can be kept at a certain temperature (25-40°C)[37] or at room temperature[28]. Another option is to centrifuge the swollen samples at a certain rpm[25]. After a while, the samples are weighted at different time intervals (minutes, hours, or weeks) depending on experiment length. Also, it can be analyzed pure water as a control sample, to compare the retention time of water for the swollen sample and the control sample, to analyze how water retention improves with the presence of hydrogel. Water retention capacity is calculated gravimetrically with the next equations(5)(6)(7).

$$WR\,\% = \frac{W_t - W_d}{W_s - w_d} \times 100 \tag{5}$$

$$WR\,\% = \frac{W_s}{W_t} \times 100 \tag{6}$$

$$WR\,\% = \frac{W_t}{W_s} \times 100 \tag{7}$$

Where: W_t represents the weight of the wet hydrogels at different intervals of time (t) during water loss, W_d is the weight of dried samples, and W_s is the weight of swollen samples.

3.2.1.2.2 Water retention of hydrogel samples in soil

To study the water retention capacity of soil with hydrogel a certain amount of hydrogel and soil samples must be weighted and prepared. The collection of a control sample (pure soil) to compare both behaviors is recommended. The prepared samples are added to the same container that could be a beaker, plastic tube, plastic pipe, plastic cup, or plastic centrifugal tubes. Then, a certain amount of water (distilled, deionized, or tap water) is added in a controlled way and weighted. The samples can be placed inside and kept in an oven with air circulation at a specific temperature (25-40°C)[34,36,39,47,56] or at room temperature[14,26,29,51,58–60]. Another option is to dry the wet samples (soil-hydrogel) using a convection dryer at 350°C[27]. The objective is generate conditions similar to summer, drought periods or extreme conditions of heat[27]. Another way could be to keep the hydrogel samples in tea bags, then immerse them in water until hydrated, later remove excess water and bury the swollen samples into the soil at room temperature[45]. The samples (soil + hydrogel) are weighed at different time intervals. The timeslots can be minutes, hours, or weeks depending on experiment length. Finally, the water retention capacity is calculated using a gravimetrical method related to the next equations(8)(9)(10)(11)(12)(13).

$$WR\,\% = \frac{W_s - W_t}{W_s} \times 100 \tag{8}$$

$$WR\,\% = \frac{W_s - W_t}{v} \times 100 \tag{9}$$

$$WR\,\% = \frac{W_s}{W_t} \times 100 \tag{10}$$

$$WR\,\% = \frac{W_t - W_d}{W_s - W_d} \times 100 \tag{11}$$

$$WR\,\% = \frac{W_t - W_c}{W_s - W_c} \times 100 \tag{12}$$

$$WR\,\% = \frac{W_t - W}{W_s - W} \times 100 \tag{13}$$

Where: W_t represents the weight of the container having the wet soil + hydrogel sample at different intervals of time (t) during water loss, W_d is the weight of containers with dry soil and hydrogels, W_s is the total weight of the water, soil, and hydrogel, W_c is the weight of the control sample (without hydrogel), W is the total weight of soil + container and v is the volume of water added to samples, taking in ml.

Note: the amounts of soil, hydrogel, and water will vary depending on the people conducting the test.

3.2.2 Evaluation of water-holding capacity and water retention capacity of the soil in hydrogel

In order to ascertain the influence of specific hydrogel formulations on soil performance, researchers study the WH and WR capacity of their materials.

Mohammadi-Khoo et al.[34] tested the WHC of soil in CBA-Cell hydrogel presence, to analyze the efficiency of hydrogel to hold water in the soil. They were prepared four samples of soil and were added different weights of hydrogel (0.05, 0.1, and 0.2g), the fourth sample was the control (without hydrogel). The results showed a WH of 38%, 52%, 65%, and 18% respectively, which demonstrates that it was an increase in water holding capacity with hydrogel presence, while the sample without hydrogel had the lowest WH. In addition, the water retention of prepared samples was also analyzed after 15 and 21 days, the results showed a WR of 16.85/1.85%, 19.98/15.47%, 32.75/29.39%, and 7.85/ 0% all the samples indicated better retention of water, when they were treated with hydrogel formulations, except in the case of the control sample, which had the lowest WR capacity and after 21 days lost all the water, the graphic representation of the results is shows in **Figure 11(a)**. It was possible to know the influence of hydrogel amount since the results showed that while the higher is the hydrogel amount, the better is the WH and WR capacity of the soil[34]. Similar results were obtained for Sarmah and Karak[46] which evaluated the WH capacity of the soil with their SAH hydrogels of starch-modified poly(acrylic acid) which were prepared varying the compositions (starch: AA wt/wt), the study demonstrated an enhance in the water holding capacity when increased the amount of hydrogel from 0.1% to 0.25%, also these results were better than control sample(pure soil) which had a WH capacity of 44%. The best water holding capacity was achieved with the SAH-2 (1:1.05) hydrogel that showed a WH capacity of 71% with 0.1% of hydrogel and a 120% with 0.25% of hydrogel, this behavior was due to the increase in porosity of the soil. SAH-1 (1:0.78) and SAH-3 (1:2.05) showed lower values of WH[46]. Zhang et al.[57] showed similar results of WH capacity evaluation, when they tested different amounts of SC-g-PAA/PAM/Urea hydrogel in soil, also it was prepared a control sample (pure soil) for comparative purposes. The results showed the largest WH capacity when the hydrogel dosage increase in the soil from 1 to 4g with a WH capacity of 47% and 161.2% respectively, this behavior is due to the high presence of hydrophilic groups within the hydrogel. The WH capacity of the soil was improved with hydrogel presence, even in small quantities in comparison to the control sample which showed the lowest WH capacity with a value of 38.7%[57].

De Guzman et al.[27] prepared four types of hydrogels from k-carrageenan, sodium alginate, and carboxymethyl cellulose varying their proportions, the samples were named P1, P2, P3, and P4. It was evaluated the percent increase in field capacity and the WR capacity of sandy loam soil and silt loam soil in presence of the hydrogels formulations and without it (control). The results showed an improvement in field capacity for both soils with all hydrogel samples, except for the control sample. The percent increase in field capacity with P1, P2, P3, and P4 hydrogels in sandy loam soil were 16.1, 7.9, 17.3, and 5.4% and in silt loam soil were 14.91, 4.96, 9.81, and 5.16% respectively at the first usage, the graphic representation of results is shown in **Figure 11(b)**. From the results is possible to say that P1 and P3 had the highest field capacity improvement, which is related to their highest swelling capacity. This improvement confirmed the potential of hydrogels to maintain higher moisture, which helps to decrease the water wasted by runoff. Also, the evaluation of water retention capacity, showed an increase in the moisture retention % with all the hydrogels samples, since a reduction in water depletion rate in sandy loam soil and silt loam soil of 17.6% and 3.9% after 2.75 days by hydrogels presence, which benefits the soil, since retains water for a longer time in unfavorable conditions. In addition, the samples were submitted to various cycles of wetting and drying test in both soils, to analyze the behavior of samples after continuous usage. The results showed that after to second and third usage of the samples the field capacity percent was improved from their repeated usage, also the drying rate decrease, which means that material can be reused[27].

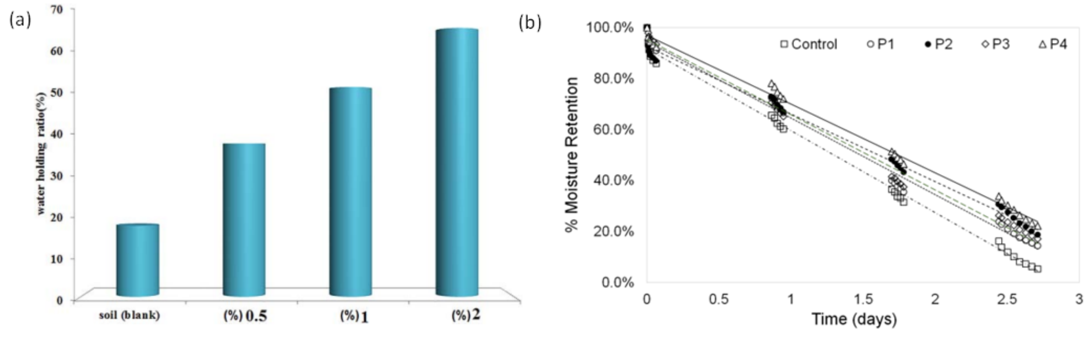

Figure 11. *(a) water retention of soil at different amounts of CBA-Cell hydrogel*[34]*. (b) water retention of sandy loam samples in presence of different k-carrageenan hydrogels*[27]*.*

In another contribution, Salimi et al.[59] evaluated the WH and WR capacity in the soil at different pH values (4.5, 5.5, and 7.5) in the presence of a series of SRF starch-g-poly (acrylic acid-co-acrylamide)/NCNps/urea hydrogels. The evaluation was performed with two hydrogel formulations SRF8 (without NCNps) and SRF10 (with the higher amount of NCNps) hydrogels, also it was prepared a control sample (pure soil). Further, it was added calcium to adapt the levels of pH for the test. The water holding results for control, SRF8, and SRF10 samples at pH 4.5 were 38, 53, 67%, at pH of 5.5 were 45, 58, 67.5%, and at pH of 7.5 were 42, 55, 58% respectively. Also, the results of water retention for control, SRF8 and SRF10 samples after 6 days at pH 4.5 were 2.0, 16.1, 35.6%, at pH of 5.5 were 5.0, 18, 33.2%, and at pH of 7.5 were 9.0, 13.6, 19.8% respectively, the graphic representation of results is shows in **Figure 12**. The decreasing in WH and WR capacity of the samples at pH 7.5 can be attributed to calcium addition since this affects the retention properties by the shielding effect of Ca^{2+} on the carboxylate groups present in the hydrogel matrix. The SRF10 showed the best results in relation to the other samples, demonstrating the absorption and retention ability to maintain big amounts of water and release it in a controlled way to the soil, the NCNps into the matrix improves the WH and WR capacity in all the studied conditions[59].

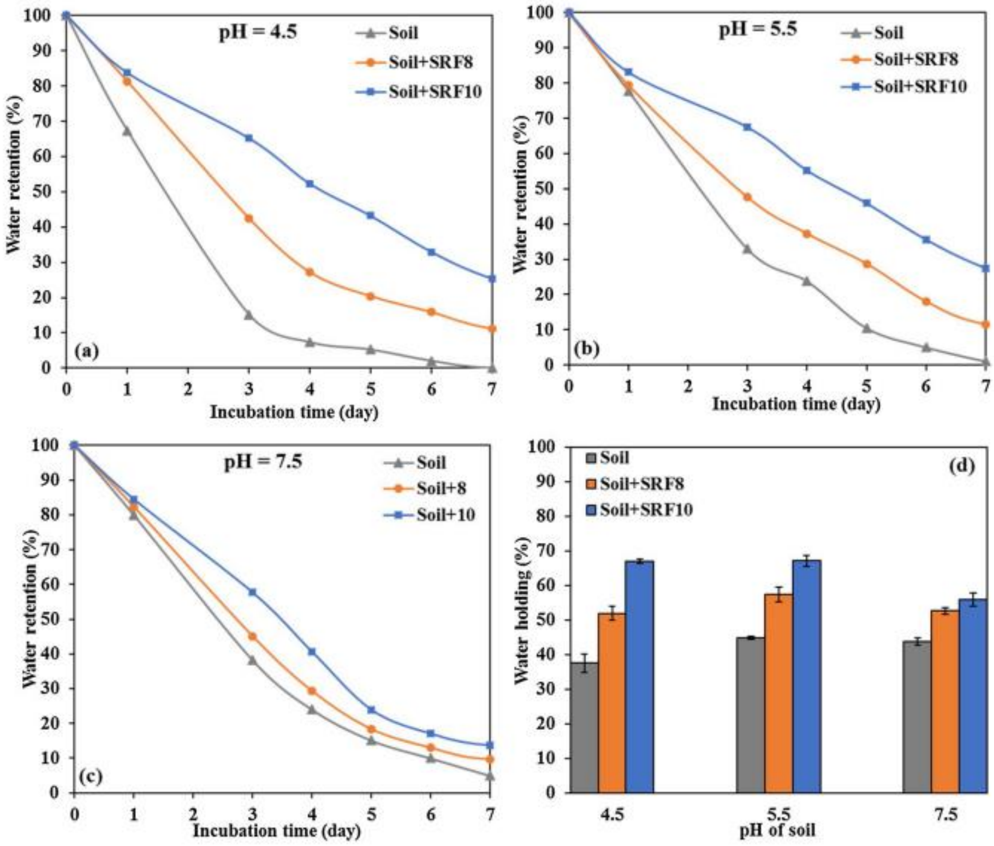

Figure 12. *(a-c) water retention and (d) water holding capacities of soil at different pH, in presence of SRF8 + soil, SRF10 + soil and pure soil samples*[59]*.*

Senna et al.[36] tested the WR capacity of the soil in presence of GEDTA/NPK and GEDTA hydrogels which are based on cellulose acetate. The evaluation was developed at 40°C to improve the soil microbial activity and chemical reactions, also it was evaluated sodium polyacrylate (SPA) and pure soil (control sample) for comparative purposes. The results showed slower evaporation for GEDTA hydrogel with or without

NPK presence in relation to the control sample, also showed that SPA in evaluated conditions is not able to retain large amounts of water, since at 40°C it loses the ability of water retention, however, showed a better WR capacity than the control sample. The water in samples GEDTA, GEDTA/NPK, SPA, and control were completely evaporated after 70h, 60h, 56h, and 53h respectively[36].

In another contribution Akalin and Pulat[14] evaluated two kinds of hydrogels CMC and CG based on sodium carboxymethyl cellulose and carrageenan respectively to know the WR capacity of the soil with hydrogel presence, also it was prepared a control sample (pure soil) to analyze the behavior of the soil. The CMC samples evaluated were CMC-1, -2, -3, and 4, the CG samples evaluated were CG-1, -2, and 3. The results showed better WR capacity in all the samples with hydrogel presence, the control sample had the lower water retention with values of 52% and 13% after 5 and 10 days. From the CMC and CG hydrogels the better WR capacity was presented by the CMC-4 sample with a WR capacity of 98% and 92% after 5 and 10 days respectively, and for CG-3 sample with a WR of 92% and 71% after 5 and 10 days respectively. The samples with the higher crosslinker content and gel content had the better WR capacity and increase water retention, from both samples CMC-4 showed the best behavior since had the higher gel level in the soil. These hydrogel formulations showed a high potential to supply and retain moisture[14].

Singh and Dhaliwal[65] prepared an MW-XG-cl-PAA/AgNPs hydrogel based on Xanthan gum (XG). The WR capacity was evaluated in clay soil, sandy soil, and a mixture of clay + sand soil in presence of hydrogel and without it as control with all the soil types. The control samples showed retain the moisture for 38, 23, and 30 days for clay, sand, and a mixture of clay + sand soil. Also, the samples with soil and hydrogel showed better water retention than control samples, since they were able to prolong the water retention where clay soil + hydrogel, sand soil + hydrogel, and mixture + hydrogel retained water for 56 days, 38 days, and 51 days respectively. The good retention capacity in clay soil is related to the size of pores since it has small particles and pores with small size, which tends to remain together and improve the moisture-holding capacity, whereas sandy soil has larger pores with big particles which facilitates the moisture loss at short times[65].

In some of the works was studied the WR capacity of hydrogel formulations without the soil presence. Sabadini and Martins[33] evaluated the behavior of their hydrated HAGG-

CH hydrogels with 4:1 and 1:1 high acetyl gella gum/chitosan (HAGG: CH) compositions, also it was evaluated the pure water retention as a control sample, the results showed that water retention of hydrogels was the twice as long than pure water. The mass was evaporated completely after 276 min in pure water and after 550 min for hydrogels formulations, the best behavior was for hydrogel with (4:1) composition which had the lowest crosslinks number[33]. In another work, Zhang et al.[37] tested the WR capacity of linseed gum/cellulose hydrogels which were prepared with different compositions. The evaluated samples were gel 4:6, 3:7, 2:8, 1:9, and 0:1. The results showed a decrease in weight retention over time, the water retention was prolonged for 14 days. The hydrogels with lower linseed gum contents presented a decrease in the weight retention ratios. Gel 4:6 showed the best water retention in relation to gel 0:1 since linseed gum help to control the sizes of pores and improve the hydrophilic property of the hydrogel matrix, while cellulose works as a backbone to bolster the porous of hydrogels. The water retention evaluation demonstrated a good water holding behavior from hydrogels[37].

Table 3. *Water holding and Water retention of hydrogels*

Superabsorbent-control sample	Evaluation	Time of retention	WR %	Evaluation	WH%	Ref
Super absorbent hydrogel HAGG-CH	Swollen sample	550 min	0% (completely evaporated)			[33]
Pure water	Pure water	276 min				
0.5% (w/w) of (CBA-Cell) hydrogel	In soil	15 days / 21 days	16.85% / 1.85%	In soil	~38%	[34]
1% (w/w) (CBA-Cell) hydrogel			19.98% / 15.47%		~52%	
2% (w/w) (CBA-Cell) hydrogel			32.75% / 29.39%		~65%	
Pure soil			7.85% / 0%		~ 18 %	
GEDTA+NPK hydrogel	In soil at 40 °C	60 h	0% (completely evaporated)			[36]
GEDTA+NPK hydrogel		70 h				
SPA (Sodium polyacrylate)		56 h				
Pure soil		53 h				
linseed gum/cellulose superabsorbent hydrogels	Swollen sample	14 days	WR can be prolonged up to 14 days			[37]
High-swelling superabsorbent composite CMC-g-poly (AA-co-AMPS)/ATP						
Hydrogel with an ATP/CMC ratio of 0.05	Swollen sample in distilled water centrifugated at 4000 rpm	10 min	74%			[25]
Hydrogel with an ATP/CMC ratio of 0.1			70%			
Hydrogel with an ATP/CMC ratio of 0.15			65%			
Hydrogel with an ATP/CMC ratio of 0.2			50%			
Super absorbent hydrogels ((CTS/Cell)-g-PAA-NPK)	In soil	12, 24, 28 days	42%, 76.25%, 82%			[39]
Pure soil			50.64%, 91.25%, 100%			
Superabsorbent nanocomposite SCMC-g-poly (AA)/PVP/Silica/NPK	In loamy sand soil	14 days / 30 days	60% / 38%			[26]
Pure soil			0% (completely evaporated) / --			
Superabsorbent hydrogel CHCAUR 4% (30% of moisture initially)	In soil at 35°C	1 h / 9 h	25% / 2%			[41]
Pure soil (30% of moisture initially)		1 h / 5 h	10% / 2%			

Poly (lactic acid)/cellulose based superabsorbent hydrogel	In red soil In white soil		Better WR in red soil than in white soil			[42]
Hydrogel k-carrageenan, sodium alginate and carboxymethyl cellulose based	In sandy loam		Depletion was reduced up to 17.6 %	In sandy loam after 1st, 2nd, 3rd usage for (P1)	16.1%, 16.7%, 31%	[27]
P1 and P3	In silt loam soil		Depletion was reduced up to 3.9 %	In silt loam soil after 1st, 2nd, 3rd usage for (P1)	14.91%, 9.3%, 21.5%	
				In sandy loam after 1st, 2nd, 3rd usage for (P3)	17.3%, 22%, 24.5%	
				In silt loam soil after 1st, 2nd, 3rd usage for (P3)	9.81%, 14.3%, 22.2%	
NaCMC hydrogels (CMC-4)	In soil	5 days / 10 days	98% / 92 %			[14]
CG hydrogels (CG-3)			90% / 71%			
Pure soil			52% / 13%			
Lipase enzyme catalyzed biodegradable hydrogel-IPN system of GT with AAm and (MAA).	In sandy loam soil	36 h	WR of soil increase in a 7%			[45]
Hydrogel IPN (up to 1%)	In clay soil		WR of soil increase in a 8%			
Super absorbent hydrogel (SAH) of starch-modified poly (acrylic acid)				In soil		[46]
SAH-1, SAH-2 and SAH-3 With 0.1 % of hydrogel					53.94% / 71% / 58.34%	
SAH-1, SAH-2 and SAH-3 With 0.25 % of hydrogel					66.81% / 120% / 81%	
Hydrogel based on alginate-poly (vinyl alcohol)	In sandy soil	2 weeks	50%			[47]
PVC/CMC Superabsorbent hydrogels	Swollen sample at room T	1 day/ 4 days / 9 days	90% / 55-75% /0%			[28]
PVP hydrogel			20% / 0% / 0%			
LR-g-PAA/MMT/Urea hydrogel	In clay soil	14 days	0% (completely evaporated)			[51]
	In a mixture of clay and sand soil	12 days				
	In sand soil	12 days				
Pure soil	In clay soil	9 days				
	In a mixture of clay and sand soil	8 days				
	In sand soil	8 days				
Urea encapsulated into salicylamide-chitosan hydrogels						[54]
CS1.5-U2 hydrogel with a WH of 154%	In soil	12 days	0% (completely evaporated)			
CS2-U0 hydrogel with a WH of 60%		12 days				
Pure soil with a WH of 29 %		7 days				

CP-g-P(AAc)/NPK hydrogel	In sandy soil	8 days / 16 days	52% / 72%			[56]
CSAP			51% / 70%			
Pure soil			71 % / 98%			
SC-g-PAA/PAM/Urea hydrogel 1 g				In soil	47%	[57]
SC-g-PAA/PAM/Urea hydrogel 4 g					161.2 %	
Pure soil					38.7 %	
WSF based in double-network hydrogels (1 g)	In sand soil	2 days / 4 days / 6 days	77.9% / 60.7% / 30.6%			[29]
Pure soil			77.8% / 58.2% / 24.2%			
BPC-g-Poly (AA)/PVA)/LDH/NP hydrogel	In loamy sand soil	16 days / 28 days	57% / 45%			[58]
Pure soil		16 days	0% (completely evaporated)			
Starch-g-poly (AA-co-AAm)/NCNps/Urea superabsorbent (SRF8) with the max of NCNPs	In soil at pH 4.5, 5.5 and 7.5	6 days	16.% / 18% / 13.6	In soil at pH 4.5, 5.5 and 7.5	53% / 58% / 55%	[59]
Starch-g-poly (AA-co-AAm)/NCNps/Urea superabsorbent (SRF10) without NCNPs			35.6% / 33.2% / 19.8%		67% / 67.5% / 58%	
Pure soil			2% / 5% / 9%		38% / 45% / 42%	
Cellulose-based hydrogel sample B2 (WH 0.54 wt%) 1 g	In soil	3 days / 5 days	19% / 5%			[60]
Cellulose-based hydrogel sample B3 (WH 1.07 wt%) 1 g			38% / 21%			
Cellulose-based hydrogel sample B4 (WH 2.12 wt%) 1 g			55% / 46 %			
Cellulose-based hydrogel sample B5 (WH 3.15 wt%) 1 g			70% / 55%			
Cellulose-based hydrogel sample B6 (WH 6.12 wt%) 1 g			45% / 30%			
B1 (Pure soil)			< 10% / 0%			
(MW-XG-cl-pAA/AgNPs) hydrogel nanocomposite 1g	In clay soil In sand soil In a mixture of clay and sand soil	56 days 38 days 51 days	0% (completely evaporated)			[65]
Pure soil	In clay soil In sand soil In a mixture of clay and sand soil	38 days 23 days 30 days				
Hyd/RHA/NPK superabsorbent nanocomposite	In loamy sand soil	10 days / 15 days	35.3% / 24.6%			[66]
Pure soil			5.6% / 0.1%			

3.3 CONTROLLED-RELEASE OF FERTILIZERS

Fertilizers use hydrogels to provide nutrients to crops in a controlled way. The use of hydrogels with the property of controlled release can substantially lower the amount of fertilizer applications required to maintain a good crop production. They also reduce the leaching of fertilizers to agricultural or groundwater overflow[27], helping reduce toxic emissions from agrochemicals that pollute the environment[15].

Slow-release of nutrients from hydrogels occurs once that hydrogels are swollen by the water or solution present in the soil, the water interpenetrates into the matrix and dissolves the soluble part of nutrients, and the molecules of nutrients are diffused slowly through the pores of hydrogel and are released into the soil[14,43]. Release behavior is determined by the capability of the ions of the nutrients, which will be transported through the network during the swelling process[47]. The hydrogel behaves like a small reservoir, which gives nutrients and moisture to the crops at a speed they are able to absorb, which provides superior results than conventional fertilizers[51]. In the real application of hydrogels to the fields, the formulation of controlled release presents a lower water content, and due to that is expected a better holding effect[52]. The controlled release of fertilizers is of vital importance to guarantee better nutrient absorption, also reduce the loss of nutrients[64].

3.3.1 Methods for fertilizer loading on hydrogels

The addition of nutrients into a hydrogel matrix can be accomplished through three different methods: in-situ technique, the two-step method (soaking method), or by a coating method.

3.3.1.1 In-situ method

It is related to the addition of fertilizer as a reagent during the synthesis of the hydrogel, this method is developed in just one step. This loading method could be developed in two ways, firstly mixing all the reagents to produce the hydrogel and then add the nutrient, and the second way is mixing the polysaccharide with nutrient in a separate container and then joining it with the rest of the reagents[40]. In the in-situ method, one of the things that must be considered is the polymerization process, to eliminate the possibility of non-reaction material or the formation of impurities into the reaction[7].

Olad et al.[26] developed a new slow-release fertilizer encapsulated by superabsorbent nanocomposite using in-situ graft polymerization for controlled release of NPK in water and soil. SCMC-g-poly (AA)/PVP/Silica/NPK (Hyd/PVP/silica/NPK) formulation was prepared with urea, ammonium dihydrogen phosphate, and potassium dihydrogen phosphate. The nutrients were dissolved in sulfonated-carboxymethyl cellulose (SCMC) solution with constant stirring and then polyvinylpyrrolidone (PVP), silica nanoparticles, acrylic acid (AA), N, N′-Methylenebis acrylamide (MBA) as a crosslinker, and ammonium persulfate (APS) as initiator were added to the mixture after 4h was completed the polymerization process, and the gel was cut in little pieces. Finally, it was immersed in ethanol and then dried in an oven at 70°C for 24h[26].

In another contribution Xiao et al.[40] prepared starch-based superabsorbent polymers (SBSAPs) for slow release of urea, using one-step process of reactive melt mixing. The hydrogel was developed in two ways. In method 1, firstly it was made the chemical modification of starch by grafting with acrylamide and then it was crosslinked with N, N′-methylene bisacrylamide (MBA) to produce the starch-based hydrogel (SBSAP), once that reaction finished Sodium hydroxide (NaOH) was added to achieve the saponification, and finally was added the urea and it was mixed. In method 2, starch and urea powder were mixing in a single process, then were repeated the same steps applied during method 1, they were obtained SBSAP/urea-M1 and SBSAP/urea-M2[40].

Shen et al.[29] performed a double network fertilizer via the ionic crosslinking of sodium carboxymethyl cellulose (CMC) and Aluminium chloride ($AlCl_3$) and the free radical polymerization of polymerizable β-cyclodextrin (MAH-CD), Acrylic acid (AA), Acrylamide (AM) and it was crosslinked with polyethylene glycol dimethacrylate (PEGDA) in a solution of urea. HNTs loaded with urea were dispersed in a solution of CMC and the urea via ultrasonication. Then the AM, AA, MAH-CD, PEGDMA, and APS, and ascorbic acid solutions as initiators were dissolved in a solution. The solution prepared previously was added a drop to drop in an $AlCl_3$ solution. Afterwards, in the $AlCl_3$ solution, it was observed the formation of spherical beads as a result of the formation of metal-carboxylate coordination bonds from the interaction between CMC and Al^{3+}. Finally, the beads were removed from the $AlCl_3$ solution through filtration and were moved to liquid paraffin. The double network water-retaining, slow-release fertilizer (WSF) beads for slow release of urea were obtained from filtration, washing, and drying[29]. The procedure of WSF preparation loaded with urea fertilizer is illustrated in **Figure 13**.

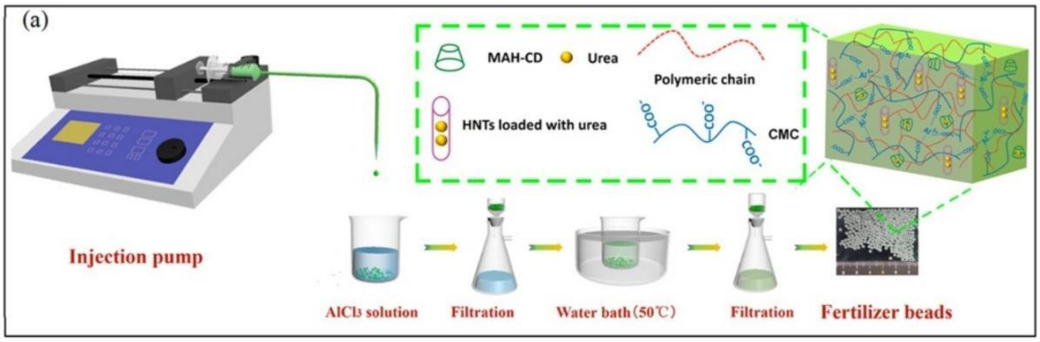

Figure 13. *Illustration of in-situ preparation procedure of WSF loaded with urea* [29].

Others controlled-release hydrogels that use the in-situ method to load nutrients were reported in the literature[14,27,55–59,61,64,66,73,30,38,43,46,49,51,52,54].

3.3.1.2 Two-step method (soaking method)

As its name indicates, fertilizer loading is accomplished in two stages. First, the hydrogel is immersed in a fertilizer solution for 24 to 72h. Second, the swollen hydrogel is dried at a temperature between 30 to 50°C[28,33–35,39,42,53,62]. This method decreases the possibility of secondary reactions into the hydrogel by the mixing all reagents in the synthesis. However, requires more steps to obtain the loaded hydrogel which implies a higher economic investment[7].

Mohammadi-Khoo et al.[34] prepared a low-cost biodegradable hydrogel based on cellulose, that was modified and crosslinked with urea, to subsequently be loaded with urea fertilizer and be released in a controlled way. Urea-modified BA-Cell hydrogel (CBA-Cell) was loaded with urea, using the soaking method. A certain amount of hydrogel was immersed in a concentrated solution of urea fertilizer and stirring slowly for 72h at room temperature until the urea swelling was complete. Finally, the loaded hydrogel was filtered, washed with distilled water, and dried at 40°C[34].

Calcagnile et al.[42] developed a fully degradable superabsorbent composite material derived from cellulose, for the slow release of potassium nitrate fertilizer that was loaded by the two-step method. The hydrogel was prepared from carboxymethyl cellulose sodium salt (CMCNa) and hydroxyethyl cellulose (HEC) which work as precursors in the hydrogel synthesis, and by poly (lactic acid) (PLA) to retard the nutrient release. It was prepared with different hydrogel samples. First, the fertilizer load was done by immersing the hydrogel formulations in different concentrations of KNO_3 solution leaving them immersed for 24h until be swollen. After, the samples were dried at 45°C for 24h to obtain hydrogel/KNO_3 (H/K). Then the PLA and KNO_3-loaded hydrogels were mixed at 190°C to obtain PLA/hydrogel/KNO_3 (PLA/H/K). Finally, the obtained blends were molded to obtain a round shape and were dried in an oven at 180°C. Also was prepared a pure PLA sample[42]. The obtained pure PLA and PLA/H/K formulations are shown in **Figure 14(a)**, where the brownish particles presented in **Figure 14(b)** appear by the hydrogel aggregates that have an appearance similar to native hydrogel powder.

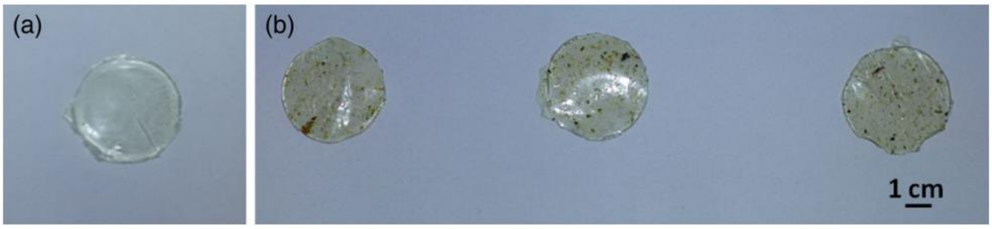

Figure 14. *(a) PLA and (b) PLA/H/K formulations obtained after two-step method for KNO_3 fertilizer loading*[42].

Saruchi et al.[45] performed a lipase enzyme-catalyzed biodegradable hydrogel interpenetrating polymer network (hydrogel-IPN), for potential controlled release application of urea and calcium nitrate fertilizers. The hydrogel was obtained from natural gum tragacanth (GT) with acrylamide (AAm) and methacrylic acid (MAA), also lipase-glutaraldehyde was used as initiator and crosslinker system to obtain GT-cl-poly (AAm) hydrogel-IPN. The fertilizers were loaded in hydrogel using the soaking method. Where first, they were prepared solutions of both fertilizers in double distilled water separately, and then an amount of dried hydrogel-IPN was immersed in the solutions during the night for the fertilizer particles enter to the matrix and the hydrogel swell. Finally, the loaded hydrogels were dried in a hot air oven[45]. **Figure 15** is an illustration of the mechanism of the nutrients loading and slow release from hydrogel-IPN.

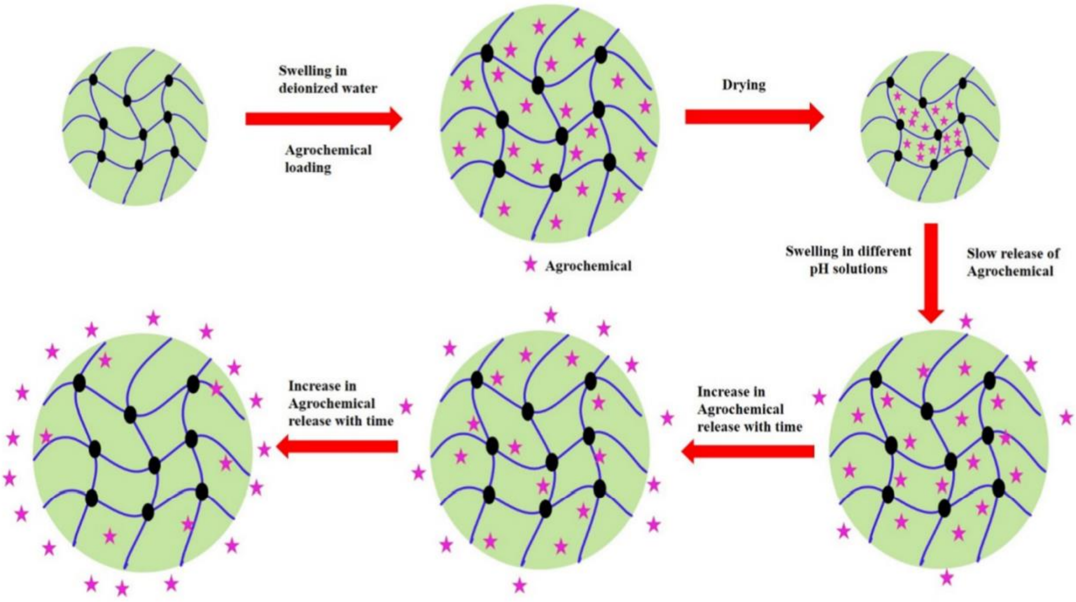

Figure 15. *Illustration of mechanisms of loading and slow release of nutrients in the hydrogel-IP*N[45].

Others controlled-release hydrogels that use the two-step method (soaking method) to load nutrients were reported in the literature[12,28,63,65,33,35,36,39,47,48,53,62].

3.3.1.3 Coating method

This method consists in using the hydrogel to encapsulate a conventional solid fertilizer. The fertilizer can have one, two, or more coats which decreases the rate of release without affection its water holding capacity. The rate of fertilizer release will be controlled by diffusion using the surface of the hydrogel as a membrane[7].

Qiao et al.[24] performed a novel double-coated slow-release of urea fertilizer from ethyl cellulose (EC) as an inner coating and starch-based superabsorbent polymer (starch-SAP) as the outer coating. The starches used were potato, maize, and cassava which were obtained from botanical origin. The starches were used to improve the water-absorbing capacity, reduce the absorbing rate, and enhance the slow-release of fertilizer. The urea load was done using the coating method, where urea granules were sieved to obtain little particles between 2-3mm, then the EC and steric acid were dissolved in ethanol. The urea granules were coated by EC solution with the help of a sprayer to form the inner layer, the samples were left to dry. After the coated granules and starch-SAP previously prepared were added to a rotating pan and the outer coating was formed. Finally, the samples were sieved to obtain the final product called potato-SAP, maize-SAP, and cassava-SAP[24]. **Figure 16** shows a schematic illustration of the (SAP) features of starch-based super absorbent polymer and the slow-release behavior of double-layer urea fertilizer.

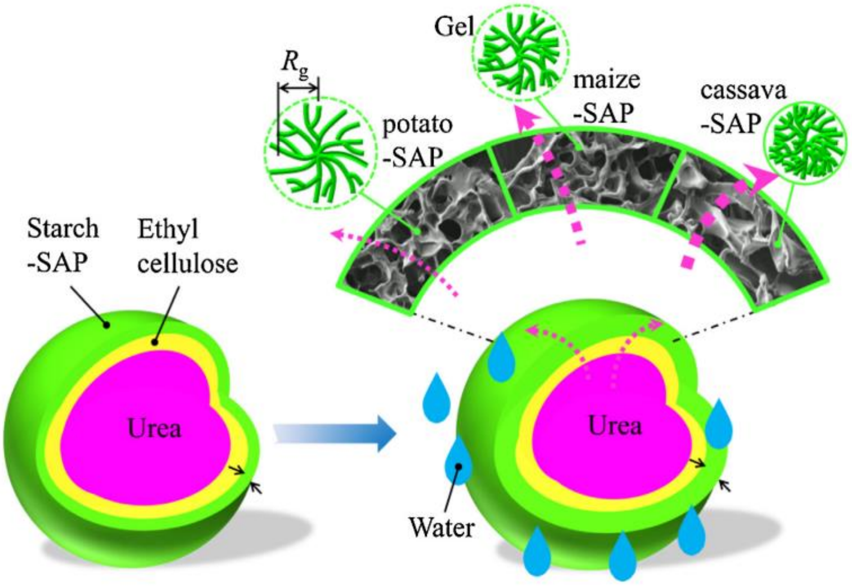

Figure 16. *Schematic illustration of the (SAP) features of starch-based super absorbent polymer and the slow-release behavior of double-layer urea fertilizer*[24].

Vudjung & Saengsuwan[15] prepared (IPN) hydrogels beads from natural rubber (NR) prevulcanized and cassava starch (St) using as crosslinkers sulfur (S) and glutaraldehyde (GA). It was developed a coating membrane IPN NR/St in solution form, for the slow release of nitrogen fertilizer. The urea bead (UB) was coated with IPN NR/St membrane as the inner layer and wax layer as the outer coating husk, to form W-IPN-CUB hydrogel. For hydrogel, development it was prepared an IPN NR/St solution, and urea beads were previously sieved to obtain a 3.6mm diameter, the solution and beads were introduced to a rotatory drum coater to be heated at 100°C and rotated at 110rpm, to obtain (IPN-CUB) samples dried. Afterwards, the samples were coated with melting wax using again the rotatory drum coater at 100rpm at room temperature and finally was obtained the (W-IPN-CUB) hydrogel[15]. The scheme of hydrogel formation in each stage is presented in **Figure 17**.

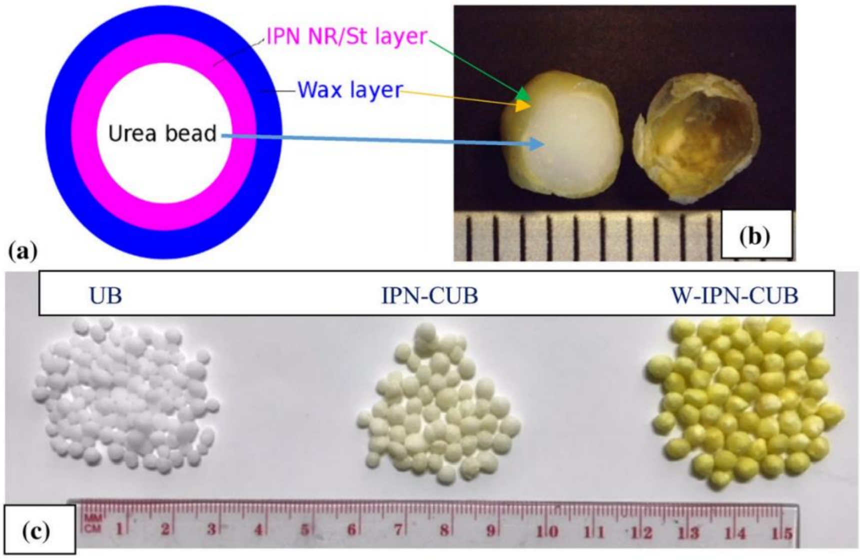

Figure 17. *(a) probable features of hydrogel, (b) optical micrograph of (W-IPN-CUB) and (c) graphic representation of (UB), (IPN-CUB) and (W-IPN-CUB)*[15].

Rozo et al.[44] reported a coating material k-carrageenan-based hydrogel (CBH) for the controlled release of nitrogen and phosphorous from granular fertilizer. Which was prepared from the mixture between an aqueous solution of k-carrageenan powder and a certain amount of glycerol which works as a plasticizing agent, the mixture was stirred continually until obtaining a clear solution. The prepared mixture was added to silicone molds and was left to cool. Before the gelation be completed, NPK fertilizers granules were added to the mold. Finally, cylindrical capsules loaded with nutrients through the coating method were obtained[44].

3.3.2 Methods for slow-release evaluation in water and soil

There is not a unique method to evaluate the slow release of fertilizers ability. The evaluation process will depend on laboratories, formulations, and the environment where the material will be implemented[52]. Most slow-release evaluations found in the literature were performed in soil and water solution and the methods used were: gravimetry, conductivity.

3.3.2.1 Gravimetric method

The fertilizer release in the water solution is calculated by determining the weight of the fertilizing in a certain amount of aqueous solution during a specific time. An amount of loaded hydrogel is kept in a volume of water solution without stirring at room temperature. At certain intervals of time, a quantity of solution from the liquid surface is moved to a previously weighed watch glass and the sample is kept in an oven until be completely dry, the watch glass is weighed again to determine the absolute weight of fertilizer. The fertilizer release percentage (FR%) is calculated using the equation(14).

$$\% \text{ FR} = \frac{\left(\Delta W_n \times \frac{(100 - (n-1) \times \blacksquare)}{\blacksquare}\right) + \sum_{i=1}^{n} \Delta W}{W_0} \times 100 \qquad (14)$$

Where ΔW_n is the weight of fertilizer released in a certain amount of solution which is represented by $\blacksquare$ symbol and W_0 is the weight of initial fertilizer in the loaded hydrogel, which is determined by the subtraction of dry loaded hydrogel weight from the initial weight of hydrogel before being loaded[34].

Another way to analyze the fertilizer release in water consists in the use of a certain amount of loaded dry hydrogel in a dialysis bag, which afterwards were immersed in an erlenmeyer flask with a water solution. After a period of time, an amount of solution is retired and analyzed to measure the fertilizer contents. The same amount of water solution that is retired from the erlenmeyer flask is added continuously to maintain constant the volume of solvent, and finally calculate the fertilizer concentration from a standard curve using the equation(15) to know the cumulative release amount.

$$\% \text{ E} = \frac{V_E \sum_{1}^{n-1} C_i + V_0 C_n}{m_0} \times 100 \qquad (15)$$

Where E is the amount cumulative released of fertilizer in percentage, V_0 is the initial volume, and V_E is the volume of sample in (ml). Also, C_n and C_i represent the fertilizer concentration in (mg/ml) and *n* and *i* are the times of sampling, and m_0 is the fertilizer content of the sample in (mg). In the case of fertilizer release in soil, it mixes a certain amount of dry loaded hydrogel with a dry soil sample with a mesh below 20 into a leaching container. Afterwards, distilled water is added to the container until obtaining saturated soil. The moisture of the soil must remain constant, so a certain amount of distilled water must be added constantly. Finally, at certain intervals the leached water is kept to analyze the content of the sample, using the above equation(15)[61].

3.3.2.2 Conductivity method

This method was used to determine the cumulative content of fertilizer released in water and soil. Dried hydrogels loaded previously with fertilizers is immersed in a certain amount of solution for a certain time, the conductivity of the solution is measured to determine the amount of nutrients released[33,39,42,53,62,63,65]. The evaluation in the soil is performed by the proper mixture of dry soil and dry hydrogel loaded with fertilizers. The mixture is slowly added to a glass column that has a ceramic membrane and a valve. Then, water is added to the soil until reaching the saturation point. The water is added constantly during the experiment period, to maintain moisture in the column. Finally, at defined time intervals, an amount of solution is collected and the conductivity is measured to determine the fertilizer content[26,66]. Sometimes the loaded hydrogel samples are kept in a bag, for example, dialysis membrane bags, before being submerged in the solution[66]. The concentration of fertilizer in the swelling medium is determined by conductance data from analyzed solutions, a calibration curve of fertilizer concentration in soil and water is made to relate the conductivity data of solution to the concentration[27,62,65].

3.3.3 Slow-release evaluation in hydrogels formulations

The terms slow-release fertilizer (SRF) and controlled release fertilizer (CRF) are normally used interchangeably since both refer to a moderate liberation of nutrients. SRF formulations will have different behavior in each plant, the performance is going to depend on the metabolic demand of the crop in question[74].

The slow-release process from hydrogels occurs in water or soil by the loaded hydrogel. This happens when the hydrogel slowly absorbed the water molecules through the pores of the surface and begin to swell, water molecules present in the release medium move towards inner layers of hydrogel, afterwards the water dissolves gradually the nutrients of fertilizer present in the hydrogel surface. By the dynamic exchange of water into the hydrogel and the medium, the dissolved fertilizer is freed slowly in the medium through the polymeric shell of swollen hydrogel network. In this phase, the release rate of dissolved nutrients is restricted by the dynamic diffusion process of water molecules, in which when the swelling ratio increases the opening size of hydrogel increases too. This behavior facilitates dissolution and the fertilizer discharged[15,26,43,66]. Initially, the freed fertilizer rate is significant by the difference of soluble material in the inner structure of hydrogel and the outer solution, but over time this difference decreases, and as result, the rate as well[26,43]. The release of nutrients in the soil from hydrogel takes place in the same way that in water. Nevertheless, it is important to emphasize, that in the soil, the diffusion of soluble nutrients from the hydrogel to the soil is more complex than in water[43].

The European Standardization Committee (CEN) developed some recommendations about SRF criteria. CEN criteria establish that fertilizer to be considered as slow-release must comply with certain parameters. First, the normal release which is related to the conversion of a chemical product into a useful tool for the plants, which can happen through hydrolysis, dissolution, or degradation. Second, the slow release, which is associated with the rate of nutrient release from the hydrogels, in which is expected a slower release of nutrients in relation to the nutrients provided by traditional fertilizers. Third, CEN states that a slow-release fertilizer can be denominated in this way if the nutrients discharge complies with certain criteria: no more than 15% of nutrients should be released within the first 24h, and the release amount should not exceed 75% within 28 days. In addition, they argue that SRFs must be profitable, environmentally friendly, and sustainable[73–75]. Not all the experimental works consider the CEN criteria. Nevertheless, by the release behavior of the hydrogels in water and soil, the people who developed the hydrogel materials are based on certain parameters to affirm a slow-release behavior.

As was presented before, the slow release of nutrients can occur from different hydrogel formulations used as transport systems, in which the soluble part of nutrients is dispersed continuously to limit the dissolution rate. The next section will analyze the release behavior of hydrogel formulations when they are tested in aqueous solutions and soil.

3.3.3.1 Slow release of hydrogels loaded with nutrients using in situ method

This method is considered one of the most cost effective and easiest processes to load fertilizers into hydrogels because the hydrogel synthesis and nutrient load occur in one step. For this reason, most hydrogels developed for slow release use this method.

Olad et al.[26] prepared a SRF based on Hyd/PVP/silica/NPK using the in-situ polymerization method. They have been made conductivity measurements as function of time in water and soil, also the release from NPK without hydrogel presence was studied. The results show that pure NPK fertilizer was completely released in 6h and 4h in distilled water and loamy sandy soil respectively. Hyd/PVP/silica/NPK formulations showed a better-sustained liberation behavior, related to the barrier effect of the polymeric matrix of hydrogel, the silica nanoparticles increased the water absorption capacity and improve the slow-release behavior. The developed hydrogel shows a NPK release of 11.2%, 32.1%, and 65.3% in water and 29%, 56.4%, 83.6 % in the soil after 1 day, 1 week, and 1 month respectively. The initial release occurs high by the facility dissolution of NPK.

From the cumulative release of nutrients in water and soil it is possible to say that hydrogel formulation freed less than 15% on the first day and did not exceed the 75% of release within the 30 days, which agrees with CEN criteria. Hydrogel formulation showed that it can increase the quantity and quality of products, also improve the fertility and water holding in the soil[26].

Akalin and Pulat[43] developed some types of k-carrageenan (k-CG) hydrogels for the controlled release of copper and manganese micronutrients. The release behavior of both nutrients was evaluated in distilled water and soil, also it was determined the number discharged of nutrients using atomic absorption spectrometry (AAS). The release in water was evaluated using the continuous release and the percent cumulative release of copper and manganese, showing results between 95-99% and 93-98% respectively, the liberation turned constant after 11-16h, the release percent of both nutrients was very closer. The release in soil was evaluated using two methods, intermittent and continuous release. From the intermittent one, the results showed a gradual increase initially, and then the release rate decrease. The discharge became constant after 8-10 days, the percent cumulative release of nutrients was between 78-88%, which showed that liberation time was around 10 times longer than the continuous release in water. The intermittent release model showed a good performance in the delivering in soil. The cumulative release of micronutrients increased with the decrease of glutaraldehyde (GA) crosslinker, which shows that crosslinking density is an important factor that influences the liberation behavior, in addition, another relevant factor is the pore size which shows, that while bigger is the size of the pore, the material swells more, but in the same way, the release of nutrients will be faster, because the loaded nutrients will escape more easily through the pores[43]. Finally, the cumulative release in soil was lower than in water. The hydrogel formulations showed to be good materials for the controlled delivery of micronutrients[43].

Shen et al.[29] formulated a double-network hydrogel for water-retaining, slow-release fertilizer (WSF) using ion-crosslinking of sodium carboxymethyl cellulose. In the hydrogel formulation was added urea-loaded halloysite as an additive. The halloysite nanotubes (HNTs) help to fit the swelling and release properties into the hydrogel. The delivery behavior of WSF with HNTs (WSF-HNTs), WSF without HNts (WSF-w-HNTs) hydrogel, and pure urea (U) was evaluated in distilled water and soil through spectrophotometry method, also in the distilled water evaluation was analyzed the influence of dialysis bag and without them during the urea release test. From the results of cumulative release (CR%) of urea in water using dialysis bag, was possible to observe a delay at the beginning of urea release, the CR% of U in water was completed in 0.5h, the CR% of WSF-w-HNTs and WSF-HNTs were of 57.8%, 75.8%, 95.4% and 48.2%, 62.9% and 86.2% after 1h, 2h, and 4h respectively. From the test results of CR% in soil was obtained that 0.5% of U was released after 0.5d, also the CR% of WSF-w-HNTs and WSF-HNTs were 59.8%, 71.6%, 98.7%, and 51.2%, 64.1%, and 95.2% after 1d, 2d and 5d respectively. The HNTs presence slower release rate of the urea in the soil because they have a higher specific surface in which some urea could be located into their cavities or adsorbed on the surface of HNTs, which in this way is hindered the nutrient release. The hydrogel formulation showed be an efficient and practical material for nutrient liberation[29].

Wang et al.[61] prepared a semi-interpenetrating polymer network fertilizer (MSP-g-AA/PVA-APP), for the slow release of ammonium polyphosphate (APP), which is based on straw cellulose and linear polymer using solution polymerization. The release of nutrients in water and soil was analyzed using the gravimetry method. The tested samples were pure APP and MSP-g-AA/PVA-APP hydrogel. The cumulative release of N and P were 76.5%, 55.3% in water, and 55.1%, 47.3% in soil, after 30 days respectively. Also, the cumulative release of pure N and P nutrients in soil and water was faster in comparison to the release of nutrients from the hydrogel. The release time of nutrients was delayed by adding products, which have a barrier effect on the network, also the release of nutrients from products was affected by the chemical bonds from the polymer chain and the steric effect, which is reflected in the good results of slow release in the soil. The hydrogel formulation showed to be ecofriendly and of low cost by the raw material used for its composition[61].

Olad et al.[66] developed a super absorbent composite for controlled release of NPK, using in-situ free-radical graft copolymerization. Hydrogel formulation was obtained from sodium alginate (NaAlg), acrylic acid (AA), acrylamide (AAm), rice husk ash (RHA), and a solution of NPK fertilizer. The delivery behavior of Hyd/RHA/NPK hydrogel and pure NPK was evaluated in distilled water and loamy sand soil, using the conductivity method to determine NPK concentration. The cumulative release results showed that release of pure NPK in water and soil was completed in 6h and 4h respectively, in the case of Hyd/RHA/NPK hydrogel the cumulative release in water and soil was 14.85% and 14.98% after 1 day and 70.4% and 71.26% after 1 month respectively. The hydrogel behavior is due to interlinked porous structures into the hydrogel network, which is obtained by the physical crosslinking effect of RHA. These structures limited the dissolution of nutrients into the matrix, and let that release occurs gradually. As the released amount of nutrients from hydrogel in water and soil does not exceed 15% on the first day and 75% after 30 days it is possible to say that hydrogel formulation complies with the established by the CEN, so it can be considered as an SRF material. The addition of RHA into the hydrogel, improve the controlled release fertilizer and the results showed, that hydrogel is an environmentally friendly material, with good slow release and water holding properties, that can be used in the agricultural field[66].

Li Xiaodi et al.[38] performed a Semi-IPNs hydrogel from wheat straw, for slow release of nitrogen and phosphorous using solution polymerization method. The WSC-g-PAA/PVA/NP hydrogel was evaluated in distilled water, NaOH solution, HCl solution, and in different salt solutions (NaCl, KCl, Na_2SO_4, and $CaCl_2$) also the results were studied using UV-visible spectrophotometer. From the release test in distilled water was obtained that hydrogel with smaller particle size (40-60 mesh) release faster than larger ones (10-20 mesh), because the samples with smaller size have a better interstitial volume and the interfacial area between swollen hydrogel and water. The release of P was around ~75% in the case of smaller particles after 20 min and in the case of larger particles after 120 min. In the case of N the release was around 66% in the case of smaller particles after 50 min and in the case of larger particles a 63% after 120 min. From the test in buffer solution and salt solution, the results suggested that cations presence let a better fertilizer diffusion coefficient, which means that cations in water increase the speed of fertilizers release own to the competition of absorption sites and competitive complexing. The delivery in salt solutions was ordered as follows: NaCl > KCl > $CaCl_2$ for N and P, where the same phenomenon of bivalent < monovalent cations presented in swelling property is repeated. Bivalent cations and water enter the hydrogel and interact with carboxyl groups, which gives as a result a denser network structure and a slower release. Slow-delivery will depend from the size of the ion radius when two monovalent or bivalent cations are the case in the case, for example, K^+ and Na^+ as K^+ has a larger ion radius will be more difficult to enter into the hydrogel network so, the competition effect for adsorption sites on hydrogel will be stronger in NaCl solutions then, the liberation of N and P was faster in NaCl than in KCl and $CaCl_2$. From the pH influence by the buffer solutions, it was obtained a P release ~73% at pH 7 and a N release of ~79% at acid medium pH 2 by the interaction of hydrogel groups and solution medium[38].

Lohmousavi et al.[58] prepared an environmental-friendly hybrid nanocomposite from Banana Peel Cellulose-g-poly (acrylic acid)/PVA and Layered double hydroxides (LDH) nanosheets, using graft polymerization for slow release of N and P. The release behavior of BPC-g-PAA/PVA/LDH hydrogel was evaluated in different salt solutions and at various pHs, and the results were studied by UV-visible spectrophotometry. The obtained results were similar to WSC-g-PAA/PVA/NP hydrogel formulated by Li Xiaodi et al.[38] the release of N increase from pH 2 to 12, and the release rate of nitrogen had a decreasing trend followed by an increase. In the case of P release, initially, the release rate increased until pH 7 and then started to decline, showing a faster release of N ~85% at a pH 2 and pH 12, and in the case of P a faster release ~75% was saw at a pH 7. From the test in salt solutions, the hydrogel formulation has a faster release of N and P in salt solutions following the next order NaCl > KCl > $CaCl_2$[58].

Salimi et al.[59] developed some bio-based SRF starch-g-poly (acrylic acid-co-acrylamide)/NCNPs/Urea for slow release of urea. The release behavior of hydrogel was evaluated in sandy loam soil using a calibrated pH meter and in deionized water, at various pHs (3-10) and salt solutions (NaCl, $CaCl_2$, and $FeCl_3$). The results were analyzed using UV-vis spectrophotometry. From the test in water was observed that samples with a higher water absorption capacity, release the N in a faster way. The hydrogels evaluation in solutions at different pH showed a slower release rate of N in basic pH, in relation to neutral solutions where the release was faster. This behavior is due to the formation of H-bonds from deprotonated carboxylic groups of hydrogel and urea which cause a slower liberation. The results from salt solutions evaluation showed a slower release than in deionized water because of the charge shielding effect of the cations, which restrict the electrostatic repulsion in the network of hydrogel, so the network is contracted, and the urea discharge is limited. The results are similar to Li Xiaodi et al.[38] and Lohmousavi et al.[58] in which the slower release rate is observed in salt solutions that contain multivalent cations. This is due to the formation of intramolecular and intermolecular complexes from the interaction between multivalent cations and COO groups in the polymer network. Hence, the release amount of urea decreases. Finally, the hydrogel formulations were evaluated in soil, the results showed that NCNPs let increase the barrier properties of the hydrogel by the formation of a tortuous path inside the polymer network, which limits the urea release in the media. Also, improve the water absorption and retention into the soil. A high number of NCNPs produces more interactions between nanoparticles and polymer which causes an intense entrapment of urea in the swelled matrix, nevertheless, after a prolonged time the strength of the gel will decrease and the interaction of the network will be weakened giving, as a result, a faster release. The hydrogel showed good properties, which make it a useful tool for agricultural fields[59].

3.3.3.2 Slow release of hydrogels loaded with nutrients using two-step method (soaking method)

This method is based mainly on two steps, in which initially the hydrogel formulation is loaded with nutrients using immersion and then is dried to be used. The soaking method is commonly used because avoids the formation of secondary reactions, nevertheless, requires a higher inversion time and expenditure of resources.

Essawy et al.[39] performed a superabsorbent made via grafting polymerization of acrylic acid from chitosan (CTS). To improve the mechanical strength of the material, it was hybridized with cellulose (Cell) via chemical bonding with thiourea formaldehyde, which allowed to enhance the flexibility of hybrid (CTS/Cell). There by as a result, the ((CTS/Cell)-g-PAA-NPK) hydrogel with strong mechanical properties and suitable for the controlled release of NPK was achieved, which was loaded using the soaking method. Controlled liberation of nutrients from ((CTS/Cell)-g-PAA-NPK) formulation and pure NPK was evaluated in distilled water with conductivity method, also it was evaluated the delivery in the soil to know the released amount of each component. N amount was analyzed using the colorimetric method based on molybdovanadate, P using a FTIR spectrophotometer and K by atomic absorption. From the results in water, it was not possible to identify the amount released for each nutrient component, nevertheless, the NPK released from hydrogel formulation was completed after 4.5h. From the results obtained in soil was found that pure NPK was almost completely released after 5 days, and in the case of ((CTS/Cell)-g-PAA-NPK) hydrogel the release of N, P, and K after 3 days was 14.67%, 12.42% and 13.67% and after 30 days 74.98%, 72.56%, and 73.23% respectively, the graphic representation is shown in **Figure 18**. These results show that superabsorbent formulation complies with the CEN criteria and the material has a slow-release behavior[39].

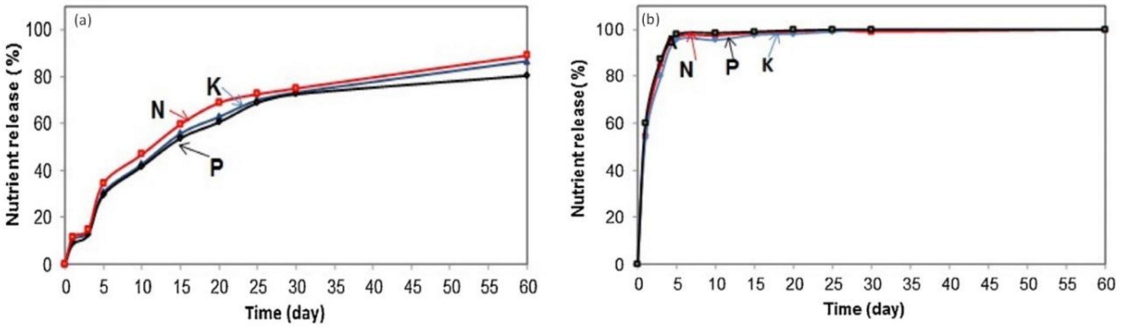

Figure 18*. release behavior of NPK in soil (a) from ((CTS/Cell)-g-PAA-NPK) hydrogel and (b) and in Pure soil without hydrogel presence*[39].

Akalin and Pulat[12] formulated a series of nanoporous from sodium carboxymethyl cellulose (NaCMC) hydrogels for the controlled discharge of copper, which was loaded using the soaking method. The hydrogel was synthesized using $FeCl_3$ ionic-crosslinker varying its amount from 4 to 10%. The slow-release behavior of NaCMC-4 hydrogel was evaluated in distilled water and soil through Atomic Absorption Spectrometer (AAS), this sample was chosen because it had the higher hydrogel formation (98%). It was prepared with a 10% of $FeCl_3$ and had a relative ratio crosslinker/polymer (C/P) of 1.43 which confers a durable and steady mechanical property. The cumulative release (%) of NaCMC-4 hydrogel in water was ~95% after 25h. The maximum release in soil was 83% after 16 days. Comparing the results in water and soil, it is possible to observe that release in water occurs 15 times faster than in soil, which means that hydrogel formulation is effective during a long time in the soil and delay the nutrient release[12].

León et al.[48] developed some hydrogels from chitosan using two approaches, oxidation under mild conditions to obtain Q_{ox} hydrogels and grafting itaconic acid to obtain Q-g-IA hydrogel for controlled release of urea, the samples were loaded using the soaking method. The hydrogels behavior was evaluated in water and at pH 12 because the soils are mainly basic, also the results were studied using UV-vis spectroscopy. The rate of both kinds of hydrogels follows the same tendency, initially, the release is very slow and then increases the release rate. The release behavior, amount of urea loaded, and swelling behavior were better in the case of Q-g-IA hydrogels. From the obtained results the urea delivery does not change from 24 to 96h, nevertheless, this released amount is a bit superior in relation to the release in water. The swelling capacity will decrease while increasing the initial concentration of urea in the media because urea presence can derange the intra and intermolecular hydrogen bonds of hydrogel, and as consequence, the amount of urea loaded will decrease with the increase of concentration. From the obtained results is possible to say that the urea discharge is better at basic pH. This has a high relevance taking into account that the soils commonly are alkaline[48].

3.3.3.3 Slow release of hydrogels loaded with nutrients using the coating method

This method basically consists of the encapsulation of fertilizers into the polymeric hydrogel, the fertilizer can be coated by one or more layers which will benefit the slow release behavior of hydrogel, since decreases the release rate of nutrients[7].

Vudjung and Saengsuwan[15] prepared a biodegradable interpenetrating polymer network (IPN) hydrogels from pre-vulcanized rubber (NR) and cassava starch (St) using glutaraldehyde (GA) as a crosslinker for slow release of nitrogen fertilizer. The W-IPN-CUB hydrogel was loaded with nitrogen fertilizer using a coating method. The hydrogel sample and pure urea beans (UB) were evaluated in distilled water and sandy soil, and the results were analyzed using UV-vis spectrophotometer. The release of fertilizer in water from pure (UB) was completed after 2h, while the release from hydrogel formulation was completed after 3 days. From the soil test was obtained that the release of fertilizer from pure (UB) was completed after 3 days in the case of hydrogel the release was completed after 24 days. The prolongation of the release in soil regarding release into the water is related to the least water molecules around the W-IPN-CUB hydrogel. From the performance of hydrogel is possible to say that it is able to be used in agriculture applications[15].

Rozo et al.[44] formulated an encapsulated k-carrageenan-based hydrogel (CBH) for the controlled release of nitrogen and phosphorous granulated fertilizers. The hydrogel formulation was analyzed in distilled water at pH 5.5 and in other solutions prepared from acetate buffer and citrate buffer with a pH of 4.5 and 6.3 through the UV-Vis spectroscopy method. From the distilled water test it was obtained that was released 17% after 1h, 23% after 24h, and 1.8% after 10min, also after 28 days they were released 95%, 68%, and 62% of NH_4^+, NO_3^- and PO_4^+ respectively. Basing on the results it is possible to say that CBH does not comply with CEN criteria, these results do not mean that CBH can not be used as CRF, just means that structure of hydrogel must be modified to preserve for a longer time the nutrients. From buffer solutions was obtained that CBH hydrogel does not present important differences in the liberation of NH_4^+ and NO_3^- at different pHs, in the case of PO_4^+ was possible to observe a delivery of 80% and 22% after 300min at a pH of 4.5 and 5.5 respectively, the results are represented in **Figure 19**. This result was obtained because of the solutions with low pH have a major positive charge of ions in the medium, which attracts the phosphate ions that are negatively charged and that are present in the hydrogel. The matrix has a negative charge by the sulfate and hydroxyl groups belonging to the carrageenan. The hydrogel formulation showed that could be a good option for CRF, to help to reduce the negative environmental impact caused for the use of fertilizers[44].

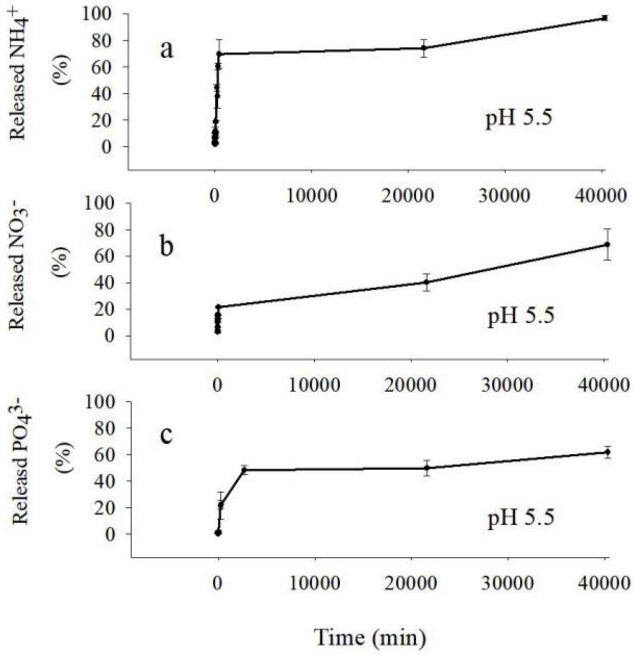

Figure 19. *release behavior of (a)* NH_4^+*(b)* NO_3^- *and (c)* PO_4^{3-} *in distilled water from CBH hydrogel*[44].

3.3.4 Factors that influence the slow-release formulation hydrogels

Hydrogel's formulations based on polysaccharides that present slow-release properties are widely used as a tool for the controlled release of water and nutrients. The main benefits of this kind of hydrogels are related to their natural resource, low cost, non-toxicities, high biocompatibility with living beings, and their environmental-friendly behavior[28,55]. The fertilizer discharge can be prolonged with the presence of hydrogel formulation, which is related to the barrier effect that produces the network[61]. The hydrogel behaves as a micro-reservoir since it is able to retain water, and also supplies the necessity of water and nutrients to the plants, showing significant advantages over traditional fertilizers[51], in addition, after hydrogel application to the soil, the water-holding capacity is improved[28]. The nutrient insertion into hydrogel contributes to the elasticity of the matrix since the interlayer space is reduced, in addition, the mechanical properties are improved by the interaction strength among polymer networks[47]. The SRF formulation is based in four principal steps. First, in the swelling of hydrogels. Second, the entry of water into the polymeric matrix. Third, the fertilizers are dissolved into the swollen hydrogel and finally, the dissolved fertilizer is diffused out of the polymer network through a dynamic interchange among the water presented into the hydrogel, and the external medium[59]. The release rate of nutrients from SRF hydrogel will be controlled by its structural characteristics and also, by the water absorbency[59]. The controlled release from hydrogel in water can be predicted since it is known that swelling degree of the matrix will be lower in electrolytes solutions than in normal water, however when hydrogel is evaluated in soil its behavior can be influenced by the type of soil, excipients, cations exchanges capacity of soil, water content, bulk density and fertilizer concentration. This could change the swelling degree of hydrogel network and therefore the fertilizer diffusion in it would be more complex and hence the release rate of nutrients decrease[39]. From literature review has been shown that polymeric network helps to delay the nutrient release to the soil because when nutrients are placed directly without encapsulation, they are faster dissolved, and their delivery after some hours is complete. Whereas when using a CRF hydrogel the release is extended for a longer period of time[52].

3.4 KINETIC MECHANISM OF SWELLING AND SLOW-RELEASE

To study the swelling process and evaluate the water absorption capacity of hydrogels swelling kinetics of water absorbency can be implemented[68]. The swelling kinetics can be studied through pseudo-first-order and pseudo-second-order kinetic models which can be applied to fit the experimental data[24,35].

Pseudo-first-order kinetic model: it is related to the absorption rate and it is associated with the number of unoccupied sites by the hydrogel. This model is represented by equation(16).

Pseudo-second-order kinetic model: it is related to the idea that absorption is associated with the square of the difference among the number of available adsorption sites in equilibrium and the filled sites. This model is represented by equation(17).

$$ln(S_{eq} - S_t) = ln\, S_{eq}(k_1 - t) \tag{16}$$

$$\frac{t}{S_t} = \frac{1}{(k_2\, {S_{eq}}^2)} + \frac{t}{S_{eq}} \tag{17}$$

Where: S_{eq} (g/g) and S_t (g/g) represents the water absorbency at equilibrium and at contact time t (min) respectively. Also, k_1 (min^{-1}) and k_2 $(g/g \cdot min)$ are the rate constants of pseudo-first and pseudo-second-order kinetic models. The correlation coefficient R^2 of the models presented and S_{eq} are parameters that let define the best-appropriated model[24,35].

3.4.1 Diffusion behavior

- Fickian transport

This model describes the type of water absorption in hydrogel networks and is represented by equation(18). To obtain the values of diffusion content (k), diffusion exponent (n) and time (t) is necessary to apply the equation(19), where n is the angular coefficient which is obtained from the slope and k is the linear coefficient which is obtained from the intercept of plot $log(M_t/M_{eq})\ vs\ log\ (t)$. The equation allows to study the effects of Fickian diffusion and viscoelastic relaxation in polymers[35,63].

$$\frac{M_t}{M_{eq}} = kt^n \tag{18}$$

$$log\left(\frac{M_t}{M_{eq}}\right) = log\, k + nlog(t) \tag{19}$$

Where k is a characteristic constant of the kind of hydrogel and swelling medium, n is related to diffusion coefficients[35] and, a parameter that gives information about the type of transport mechanism that describes the water diffusion into the hydrogels[34,63]. M_t and M_{eq} are the masses of hydrogel at swelling time and at equilibrium state respectively, when $M_t \leq 0.7 M_{eq}$ and when $M_t > 0.7\ M_{eq}$ the linear behavior represented by the equation(19) it is not keept in the last stages of absorption[63]. The equation must be applied at the initial stages, until around 60% of the swelling because at this stage, the increase of swelling degree over time is a straight line that ascends[34]. M_t/M_{eq} is the fractional uptake of water normalized with respect to the equilibrium conditions.

When $n \leq 0.45$ shows a Fickian diffusion transport, at n values between 0.45 to 0.85 show a non-Fickian diffusion transport, at n values = 0.85 show a case II transport, and finally when $n > 0.85$ water transport occurs exclusively by macromolecular network relaxation[35,55,63].

In Fickian diffusion, the water molecules diffuse by the hydrophilic porous network of hydrogel only through the diffusion process. Non-Fickian diffusion is characterized by two processes that occur simultaneously, first the diffusion through pores and second the macromolecular network relaxation of the hydrogel network[55,63].

- Schott's second order:

  This model is applied to understand the swelling behavior of hydrogel. It is represented by equation(20). From the plot of t/Q_t vs t is possible to obtain the M_{eq} and K_{is} which are the slope and intercept respectively, also the graphs could show a straight line and the correlation coefficient R^2, it lets analyze if this model is appropriated to describe the behavior of hydrogel, while closer to 1 is R^2 major fitting the data present[29,38,51,58].

$$\frac{t}{M_t} = \frac{1}{k_{is}} + \frac{t}{M_{eq}} \tag{20}$$

where M_{eq} and M_t as was mentioned before represent the masses of the hydrogel at the swelling time and at time t, also k_{is} indicates the initial swelling rate constant $(g/g \cdot min)$[29]. The swelling rate of hydrogels is highly related to the osmotic pressure of the medium in which sample is immersed, also with the relaxation rate of chain parts in the network[57].

Some experimental works evaluated the swelling and slow release kinetics of the prepared hydrogels, and most of them shown that the diffusion mechanism that their material was related to Fickian transport, and some materials show a Schott's second order diffusion, this behavior is presented in **Table 2** and **Table 4**.

Table 4. *Slow-release behavior of hydrogels in water and soil*

Active principle	Load methodology	Evaluation	Superabsorbent-Control sample	Time of release	Amount released	Kinetic method	Ref
MKP fertilizer	Two-step method	In pure water	Superabsorbent hydrogel HAGG-CH (1:3)	8h	~450 mg/g		[33]
			Superabsorbent hydrogel HAGG-CH (4:1 and 1:4)	8h	~400 mg/g		
Urea fertilizer	Two-step method	In distilled water	*Urea-modified BA-Cell (CBA-Cell) hydrogel	1 day	22.9%	Kormeyer-peppas and Ritger-peppas models	[34]
				21 days	95.71%		
				30 days	97%		
Humic acid fertilizer	Two-step method	In distilled water at pH (4.5-10.5)	Novel and eco-friendly chitosan/yeast hybrid hydrogels bead	300 min	82.6% at pH 7.5		[35]
NPK fertilizer	Two-step method	In soil	GEDTA hydrogel		237.5 mg/dm^3 of NH_4^+ 240 mg/dm^3 of K^+ 13 mg/dm^3 of $H_2PO_4^-$ at 475 mm/m^2 irrigation		[36]
Nitrogen and phosphorous nutrients	In-situ method	In distilled water	Wheat straw based Semi-(IPNs) hydrogel	120 min	~75% of P and ~65% of N	First order release	[38]
		In NaCl solution			~70% of P and ~67% of N		
		In KCl solution			~65% of P and 70% of N		
		In CaCl2 solution			< 65% of P and ~62.5% of N		
		at pH 6-8			~72.5% of P and ~66% of N		
		at pH 2			~63.5% of P and ~79% of N		
Urea-N2 fertilizer	Coating method	In soil	Uncoated urea	24h	95%		[24]
			Novel dual-layer slow-release nitrogen fertilizer Starch-SAP		40%		
			Novel dual-layer slow-release nitrogen fertilizer Potato-SAP	96h	70%		
NPK fertilizer	Two-step method	In sandy soil	Super absorbent hydrogels ((CTS/Cell)-g-PAA-NPK)	3 days	14.67% N, 12.42%P, 13.67K		[39]
				5 days	34.64% N, 29.54%P, 30.56K		
				30 days	74.98% N, 72.56%P, 73.23K		
		In distilled water		4.5 days	100% of NPK		
		In sandy soil	Pure NPK	5 days	100% of NPK		

NPK fertilizer	In-situ method	In loamy sand soil	Hyd/NPK	1 day, 1 week and 1 month	14.6%, 27.6%, and 54.6%	Fickian diffusion	[26]
			Hyd/PVP/NPK	1 day, 1 week and 1 month	16.7%, 34.6% and 72.3%		
			Hyd/PVP/silica/NPK	1 day, 1 week and 1 month	29%, 56.4% and 83.6		
			Pure NPK	4h	100% of NPK		
		In distilled water	Hyd/NPK	1 day, 1 week and 1 month	31%, 62.1% and 89%		
			Hyd/PVP/NPK	1 day, 1 week and 1 month	16.9%, 44.5%, and 75.3%		
			Hyd/PVP/silica/NPK	1 day, 1 week and 1 month	11.2%, 32.1% and 65.3%		
			Pure NPK	6h	100% of NPK		
Urea fertilizer	In-situ method	In tap water	SBSAP/Urea M1	30 days	77.33%		[40]
			SBSAP/Urea M2	30 days	71.20%		
				0-5 days	< 15%		
				5-20 days	> 50%		
				20-40 days	> 80%		
				> 45 days	Material loss strength and was disintegrated		
Nitrogen Fertilizer	Coating method	In sandy soil	Pure urea bean	72 h / 3 days	100%	Modified peppas's model	[15]
			W-IPN-CUB hydrogel	576 h/ 24 days			
		In distilled water	Pure urea bean	2h			
			W-IPN-CUB hydrogel	72h			
KNO3	Two-step method	In water	Poly (lactic acid)/cellulose based superabsorbent hydrogel				[42]
			H/K100	6 h	90%		
			PLA/H10/K100	168 h	80%		
NPK fertilizer	In-situ method	In distilled water	Hydrogel k-carrageenan, sodium alginate and carboxymethyl cellulose based				[27]
			P3-hydrogel	3 days	53%		
Copper and manganese	In-situ method	In soil	K-carrageenan (k-CG) hydrogels	Cumulative release	80-88%	Case II, relaxation transport	[43]
						Zero order model	
		In distilled water		Intermittent release	80-88%		
NPK fertilizer	Coating method	In distilled water	K-carrageenan-based hydrogel (CBH)	1h and 28 days	17% and 95% of NH_4^+	Korsmeyer-Peppas model	[44]
		at pH 5.5		24h and 28 days	23% and 68% of NO_3^-	non-Fickian diffusion	
				10 min and 28 days	1.8% and 62% of PO_4^{3-}		

		In buffer solution					
		at pH 4.5		300 min	80% PO_4^{3-}		
		at pH 5.5		300 min	22% PO_4^{3-}		
Zinc Nutrient	In-situ method	In soil	NaCMC hydrogels (CMC-4)	3 days, 5 days, and 10 days	13.5%, 25.3% and 65.3%		[14]
		In distilled water	NaCMC hydrogels (CMC-4)	3 days, 5 days, and 8 days	20,5%, 38,7%, and 66,7%		
		In soil	CG hydrogels (CG-1)	3 days, 5 days, and 10 days	40.3%, 60.1% and 91.3%		
		In distilled water	CG hydrogels (CG-1)	3 days, 5 days, and 8 days	50,4%, 71,4%, and 96,1%		
Urea and calcium nitrate	Two-step method	In distilled water	Lipase enzyme catalyzed biodegradable hydrogel-IPN system of GT with AAm and (MAA).	4 h	37.44 ppm of urea 64.2 ppm of calcium nitrate	Case II diffusion	[45]
				44h (In equilibrium)	722.8 ppm of urea 1151.64 of calcium nitrate		
Urea fertilizer	In-situ method	In tap water	Super absorbent hydrogel (SAH) of starch-modified poly (acrylic acid)	1-5 days	25% of urea		[46]
				5-20 days	> 64% of urea		
				20-30 days	> 90-99% was released		
Zinc nitrate	Two-step method	In deionized water	Hydrogel based on alginate-poly (vinyl alcohol)	12 days	69.25% of Zn (2+)		[47]
Urea, NPK and MPK	Two-step method	In distilled water	PVC/CMC Superabsorbent hydrogels	1 day	29 mg/ml of urea and 1.5 mg/ml phosphate		[28]
				2 days	23.3 mg/ml of urea and 1.5 mg/ml of phosphate		
				3 days	21.8 mg/ml of urea and 2.4 mg/ml of phosphate		
				4 days	14.7 mg/ml of urea and 3.1 mg/ml of phosphate		
Urea fertilizer	Two-step method	In deionized water	Chitosan- based Q1-g-IA superabsorbent hydrogel (1/1 chitosan/IA)	96h	Urea concentration 70 ppm-initial urea release of 24.4 ppm Urea concentration 100ppm-initial urea release of 29.7 ppm		[48]
		In solution at pH 12			Urea concentration 130 ppm-initial urea release of 95 ppm Urea concentration 100ppm-urea release of 50 ppm		
Copper nutrient	Two-step method	In soil	(NaCMC) hydrogels	16 days	83%	Zero order kinetic	[12]
		In distilled water		25 h	95%		

CuSO4	In-situ method	In distilled water	Cs/PAA/Cu/3%-HNCs hydrogel nanocomposite	25 h	90%		[49]
Urea fertilizer	In-situ method	In soil	(LR-g-PAA/MMT/Urea) hydrogel		leaching loss of N 19.7%		[51]
			Pure urea		leaching loss of N 52.3%		
Urea fertilizer	In-situ method	In soil	CaCO3-reinforced PVA-SA hydrogel		60%		[52]
Urea, KNO3 and NH4NO3	Two-step method	In distilled water	Superabsorbents starches (SASs) CMUS	100h, 320h and 320h	Urea 2g/l 35%, KNO3 10g/l 75% and NH4NO3 0.5 g/l 30%	First order release	[53]
			Superabsorbents starches (SASs) CMES	100h, 320h and 320h	Urea 2g/l 45%, KNO3 10g/l 65% and NH4NO3 0.5 g/l 85%		
			Superabsorbents starches (SASs) CCS	100h, 320h and 320h	Urea 2g/l 75%, KNO3 10g/l 80% and NH4NO3 0.5 g/l 95%		
Urea fertilizer	In-situ method	In distilled water	Urea encapsulated into salicylimine-chitosan hydrogels (CS2-U2 hydrogels)	5 h	46.8%	Urea was released in 3 stages	[54]
				1 day	50%	1.- burst release-non-Fickian diffusion	
				11 days	89.5%	2.- prolonged release-Fickian diffusion	
				35 days	100%	3.-release of the remanent urea	
Phosphorus	In-situ method	In distilled water	AGBH and AGBCH hydrogels reinforced with eucalyptus and pinus residues	0-500 min	Increase in the amount of nutrient released	Fickian transport	[55]
				960-2800 min	No significant		
NPK fertilizer	In-situ method	In distilled water	Coco peat-grafted-poly (acrylic acid)/NPK [CP-g-P(AAc)/NPK] hydrogel	180 min	38.1%		[56]
				1 day	90.1%		
				5 weeks	100%		
			Pure NPK	45 min	30%		
				105 min	100%		
Urea fertilizer	In-situ method	In deionized water	SC-g-PAA/PAM/Urea hydrogel	10 min	2.6%	Using Ritger-Peppas release model	[57]
				30 min	8.6%	Case II release	
				480 min	82.4%		
Urea fertilizer	In-situ method	Sandy soil	WSF hydrogel based in double-network hydrogels	1 day, 2 days and 5 days	51.2%, 64.1% and 95.2%	Peppas model-Fickian diffusion	[29]
			Pure urea	0.5 days	100%	Higuchi model-shows that hydrogel does provide slow release of urea	
		Distilled water	WSF hydrogel based in double-network hydrogels	1 h, 2 h and 4h	57.8%, 75.8% and 95.4%	First order kinetic model	
			Pure urea	0.5 days	100%		

NPK fertilizer	In-situ method		Super absorbent NaCMC-poly (AA-co-Aam hydrogel modified by rice husk	6 days			[30]
		In 0.9 NaCl solution	SC3 with 3wt% of NaCMC		50%		
			SC9 with 3wt% NaCMC, 15% RHA and 5% NPK		25.15%		
		Distilled water	SC9 with 3wt% NaCMC, 15% RHA and 5% NPK		25.20%		
Nitrogen and Phosphorus	In-situ method	At pH 3, 12	BPC-g-Poly (AA)/PVA)/LDH/NP hydrogel		85% of N		[58]
		At pH2, 12			60% of P		
		At pH 7			70% of N and 75% of P		
		In CaCl2 solution		120 min	62% of N and 65% of P		
		In NaCl solution			70% of N and P		
		In KCl solution			68% of N and 60% of P		
Urea fertilizer	In-situ method		starch-g-poly (AA-co-AAm)/NCNps/Urea superabsorbent polymer	21 days			[59]
		In distilled water	SRF5		95%	SRF5 Non-Fickian diffusion mechanism	
		In deionized water	SRF8, SRF9 and SRF10		87%, 71% and 73%		
		At pH 10	SRF8 and SRF0		50%		
		In 0.001 M NaCl	SRF8, SRF9 and SRF10		44%, 31% and 37%	Other samples	
		In 0.001 M CaCl2	SRF8, SRF9 and SRF10		30%, 25% and 24%	Fickian diffusion mechanism	
		In 0.001 M FeCl3	SRF8, SRF9 and SRF10		25%, 15% and 18%		
APP and urea	In-situ method	In soil	Novel semi-IPNs (MSP-g-AA/PVA-APP) hydrogel	30 days	55.1% of N and 47.3% of P	Korsmeyer-Peppas model Fick diffusion and polymer chain relaxation	[61]
		In distilled water		30 days	76.5% of N and 55.3% of P		
KNO3 and NH4NO3	Two-step method	In distilled water	A series of carboxymethyl sago pulp (CMSP) hydrogels	2 days	50% of KNO3 and 50% of NH4NO3	Fickian diffusion and non-Fickian diffusion	[62]
				< 10 days	60-70% of KNO3 and 60-85% of NH4NO3		
				50 days	80-90% of KNO3 and 86-92% of NH4NO3		
Potassium, phosphate, and ammonia	Two-step method	In pure water	Arabic gum-based hydrogel (MAGBH)	1440 min	96,1 % of Potassium 16.3% of Phosphate 11.5% of ammonia		[63]
K2HPO4	In-situ method	In distilled water	HCG and HCGP Super absorbent hydrogels (SAHs)	4h	25.5 mg/L (in equilibrium)	Korsmeyer-Peppas model Fickian diffusion mechanism	[64]
KCl	Two-step method	In deionized water	(MW-XG-cl-pAA/AgNPs) hydrogel nanocomposite	80 h	1200 ppm	Korsmeyer-Peppas model	[65]

						non-Fickian diffusion	
NPK	In-situ method	Loamy sand soil	Hyd/RHA and Hyd/RHA/NPK superabsorbent nanocomposite	1 day, 1 week and 1 month	14.98%, 31.86% and 71.26%		[66]
		distilled water			14,85%, 29.36% and 70.4%		
		Loamy sand soil	Pure NPK	4h	100%		
		distilled water		6h	100%		

3.5 BIODEGRADABILITY

The main objective of hydrogels formulations for the slow release of nutrients is to supply nutrients in a controlled and prolonged way to satisfy the necessities of the plants[15]. The stability of the matrix structure plays an important role since a stiffer matrix would restricts the hydrogel's ability to swell, hold water, and make it harder to degrade; while a loose matrix might dissolve in the medium too quickly[43,49]. In the case of hydrogels developed with polysaccharides, their hydrophilic groups grant the ability to improve the swelling capacity and degradation with the help of microorganisms. In addition, the efficiency of the material will depend on some environmental conditions as temperature and pH which influence the hydrogel performance[45,49]. Soil will be directly affected by non-biodegradability, since in the case of synthetic materials they are degraded very slowly, generating pollution[46].

3.5.1 Methods for the evaluation of biodegradability

There are some evaluation methods to determine the biodegradability of hydrogels the most common is the weight loss of the samples, burial method, composting method, or broth culture.

3.5.1.1 Immersion method

This method consists in swell the hydrogels samples in a water solution of (*PBS or *BRB) and let them rest for a certain time which could be hours or days at pH 7 and 30°C[12,43]. Another option is swelling the samples with distilled water and dry them in an oven for 24h at 105°C[49]. Then the swollen samples are removed from the solution and weighted. After, the samples are immersed in the same medium, and they are weighted every so often, until that they are completely degraded. Finally, basing on weight loss it is calculated the degradation of samples[12,43,49].

*Phosphate-buffered saline(PBS)[43].

*Britton-Robinson buffer (BRB)[12].

3.5.1.2 Burial method

This test consists of taking a certain amount of hydrogel samples and bury them at a certain distance from the soil surface (7-9cm)[15,46], also the hydrogel samples can be wrapped in a material before being buried, which can be a nylon fabric or tea bag[59]. A determined amount of water must be added every so often for a determined period. The water levels of samples must be maintained in a proper way to prevent any leak, periodically the samples are recollected carefully, washed with water (distilled or deionized water), and dried at a determined temperature (45-70°C)[15,56,62], the samples are weighted once that their weight remains constant. The biodegradability is determined by the weight loss of the samples, the weight of the samples is averaged to define the weight[15,45,46,56,59,62].

Biodegradation with soil burial method can be divided into three stages: The first stage is related to the degradation of biological matter of hydrogel, which occurs by the presence of the microorganisms in the soil, which improve and accelerates the decomposition process[46]. In the second stage, the degradation slows down, by the increase of water content into the matrix. Which hamper the oxygen transference to the hydrogel network and generate an anaerobic medium that decreases microbial development and therefore the degradation takes longer[46]. In the third stage, the hydrogel starts to decompose in smaller fragments, which facilitates microbial attack and enhances decomposition[46].

3.5.1.3 Composting method

Composting method is similar to the burial method, the unique difference is that instead to use fresh soil to the test, it is used a compost sample[45]. Composting is a natural way to recycle organic waste, which comes from residues of food and crop waste, which can be used to improve the soil and plants yield[76]. Remove these residues represent a great investment of economic resources and a big effort for the environment to undo. Compost lets accelerate the degradation process giving an ideal medium to improve the generation of bacteria, fungi, or another decomposing organism. These residues work as compost in the soil and in agricultural media is known as "black gold"[76].

3.5.1.4 Broth culture method

The Broth culture method can be developed using the McFarland turbidity standards is used to study the concentration of bacterial strains in an aqueous medium, which can be determined using the turbidimetry technique. The microbes absorb and scatter the incident light, and consequently, the measured absorbance (turbidimetry) is directly proportional to microbes concentration in the medium[77]. The test is developed with a series of tubes which must be calibrated previously with an optical density. McFarland standards are used as turbidity patterns for microorganisms suspensions[78]. The absorbency obtained is compared with the absorbance of the bacterial population[77,78].

The broth culture method consists of the biodegradation study of hydrogel samples against bacterial strains through the McFarland turbidity method. In which first is prepared a nutrient medium in distilled water, by the addition of certain compounds as $(NH_4)_2SO_4$, KH_2PO_4, etc. The culture media previously prepared must be sterilized in an autoclave under certain conditions, after is let cooling at room temperature. The nutrients solution is used to culture the bacterial strain in an incubator at a determined temperature and a period. Microbes samples are taken from a culture medium and are sterilized under UV exposure. The hydrogel samples are immersed in the culture medium with the bacterial strain at sterile conditions. Also, a control sample must be prepared for comparative purposes. Biodegradation is evaluated by studying the bacterial growth in the samples, which is determined through absorbance and optical density (OD) measurements and compared to the control one. Finally, the weight loss of hydrogel samples is measured after a certain period to know the biodegradability level of the material[46].

Degradation level is calculated based on the weight loss of samples, the same equation(21) can be used for all the methods described above.

$$Weight\ loss\ \% = \frac{W_i - W_f}{W_f} \times 100 \qquad (21)$$

where W_i represents the initial weight of before degradation and W_f is the weight of samples at different intervals of time (t) during the degradation process. Each time that samples are extracted and weighed, they can be analyzed through SEM and FTIR to observe the hydrogel at different stages of biodegradation[15,45].

Note: the amounts of soil, hydrogel and water will vary depending on the people conducting the test.

3.5.2 Biodegradability evaluation of hydrogel formulations

Akalin and Pulat[43] studied the biodegradability through the immersion method of a series k-CG hydrogels which were crosslinked with GA. The samples were swollen with PBS at pH 7 and 30°C. The degradation was determined by weight loss in the samples. The results showed that samples with a higher crosslinking amount delay a longer period to be degraded in relation to hydrogels with a low crosslinking amount. For this reason, sample CG-1 was degraded after 4 days (lower gel content and crosslinker content) whereas sample CG-6 was degraded after 8 days (higher gel content and crosslinker content). All the studied samples lost 100% of their weight in a period between 4 to 8 days. The results demonstrated that a high crosslinking density forms more durable hydrogel structures, with lower swelling capacity and that, require a longer time to be degraded[43].

In another contribution Akalin and Pulat[12] prepared some NaCMC hydrogels crosslinked with $FeCl_3$, they evaluated the degradation of samples using the same method and conditions described above, except that in this test the samples were swollen with BRB. The result showed the same tendency that k-CG hydrogel, where NaCMC hydrogels with lower crosslinker amount were degraded faster than hydrogels with high crosslinker amount, all the evaluated hydrogels were degraded in a period between 33 to 38 days. Where NaCMC-1 showed the faster degradation in 33 days and NaCMC-4 the slower degradation after 38 days. The crosslinking density plays an essential role in degradation since a large amount of crosslinker improve the number of intermolecular bonds forming more durable and steady samples, whereas lower crosslinker quantities form brittle structures with an easier degradation.

Abd El-Aziz et al.[49] evaluated the biodegradation behavior of CS/PAA/HNCs hydrogels which were synthesized through ionic gelation and copolymerization, the test was performed by immersion method in distilled water, also for comparison purposes was evaluated CS-NPs . The hydrogels were load with different amounts of copper ($CuSO_4$) from 1-3%. The results showed a decrease in degradation when increase the copper amounts own to release of copper in water after immersion. CS/PAA/HNCs hydrogels were degraded faster than CS-NPs by the size effect of chitosan hence the hydrolysis of nano chitosan accelerate the degradation. After 24h the CS/PAA/HNCs and CS-NPs hydrogels without copper are degraded in a 50% and 30% respectively while the samples with the higher load of copper (3%) were degraded in a 30% and 10% respectively[49].

Some of works evaluated their hydrogel formulations using burial method. Vundjung and Saengsuwan[15] studied the degradation behavior of a series of W-IPN/St hydrogels in the soil each week for 90 days using the buried method, also the morphology of the samples was studied too through SEM analysis after 30 and 90 days. The hydrogel samples were developed varying their NR/St ratio (100/0, 90/10, 80/20, 70/30, and 50/50), the results showed a higher weight retention % in samples with lower St (sample 90/10 ratio), while the samples with higher St were degraded faster (sample of 50/50 ratio). After 90 days the weight retention of hydrogels decreased from 83 to 48% when increasing the St content from 50 to 90%. NR molecule is degraded by St action since St has a hydrophilic behavior that increases the hygroscopic characteristics of hydrogel and improves the microorganism development in the degradation process. Three hydrogel samples (90/10, 70/30, and 50/50 ratios) were evaluated through SEM after 30 and 90 days, the results showed an increase in degradation over time. After 30 days the samples presented some perforations on the membrane surface, while bigger was the St content in the sample, major was the number of holes. After 90 days the holes had a bigger size in all the samples and was remarkable their presence in the structure[15].

Saruchi et al.[45] prove the biodegradation behavior of hydrogel-IPN based in GT with AAm and MAA which were developed using graft co-polymerization. Degradation tests were performed through the burial and composting method for 11 weeks, also the samples were studied through SEM and FTIR techniques. The results showed a complete degradation after 77 days from the composting method, whereas with the soil burial method the 81.26% of the sample was degraded after 77 days. This behavior is related to the various types of micro-flora presented in soil and compost which improve the degradation process, in the case of composting the micro-flora is higher in relation to fresh soil which lets it a faster degradation. From the SEM results of samples tested with the burial and composting method, it was possible to identify certain changes in the surface of the hydrogel structure. After the first week, the samples presented superficial cracks, after six weeks, the morphological damage increased and was notable the growth of cracks, also the pits were deepened, finally, after 11 weeks the samples presented a complete breakdown of samples, degradation process is represented in **Figure 20**. From

FTIR analysis were compared the spectra of hydrogel used during the degradation process. After the first week was possible to observe some peaks shifted to other positions and a reduction in the intensities of the peaks caused by crosslinks breakdown into the network by the microorganism attack. After 6 weeks the intensities of peaks decrease more and others disappear, by the degradation of individual components of the hydrogel. After 11 weeks, the old peaks disappeared by degradation process and appear new peaks by subproducts formation. The changes in morphology by degradation show that crosslinking and grafting did not affect the eco-friendly behavior of GT polysaccharides[45].

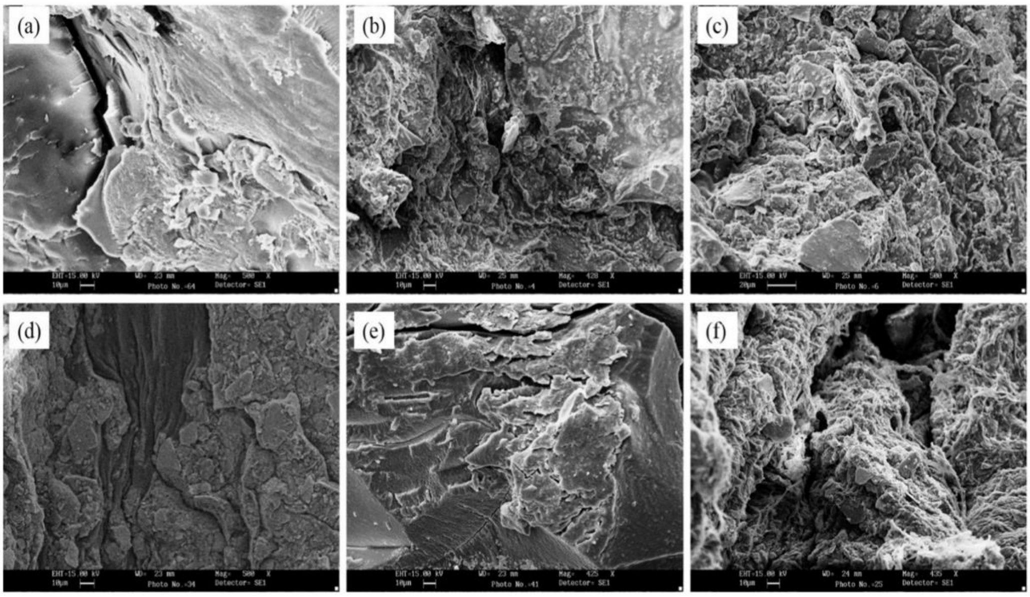

Figure 20. *SEM images of Hydrogel-IPN during degradation process (a-c) from composting method, (d-f) from burial method after 1, 6 and 11 weeks respectively*[45]**.**

Sarmah and Karak[46] evaluated the biodegradation performance of their SAH hydrogels from starch-modified poly(acrylic acid) through broth culture method during 6 weeks and burial method during 3 months. The burial test was evaluated in sandy soil at pH 6.5, while the broth culture method was developed against *Pseudomonas aeruginosa* (gram-negative) and *Bacillus subtilis* (gram-positive) bacterial strains through the McFarland turbidity method. The evaluated samples were SAH-1, SAH-2, and SAH-3 which have different compositions of reactants, also PAA hydrogel as a control sample. The obtained results from the broth culture test show that all the samples were degraded gradually by bacterial strains by exposure in culture media. The biodegradation was determined by bacterial growth through OD of bacterial strains at an absorbance of 600nm which showed the turbidity of the medium. The difference in the degradation of polymer hydrogels is related to the difference in the cell wall of gram-positive and gram-negative bacteria. Biodegradation rates follow the next order SAH-1 > SAH-2 > SAH-3 > PAA, where SAH-1 had the highest amount of starch in the network, which eases the growth of both bacterial strains and SAH-3 the highest gel content which decreases the bacterial growth. Whereas PAA hydrogel did not show significant signals of degradation due to its synthetic part in the conformation. Weight loss % of samples after 6 weeks of microbial attack was 57%, 55%, 35%, and 10% for SAH-1, SAH-2, SAH-3, and PAA respectively. The results from the burial test showed the same tendency of degradation as broth culture. The weight loss % of samples after 3 months was 40%, 33%, 28% and 5% for SAH-1, SAH-2, SAH-3 and PAA respectively[46].

Table 5. Biodegradability Evaluation of hydrogels

Type	Polysaccharide	Type and name of superabsorbent	Evaluation method	Time of degradation	Weight loss %	Ref
Natural-modified	Starch	Interpenetrating polymer networks (IPN NR/St) Hydrogel	Burial method	90 days	100% (completely decomposed)	[15]
Natural-modified	k-carrageenan	K-carrageenan (k-CG) hydrogels	Immersion method at pH 7 and 30 °C	4-8 days	100% (completely decomposed)	[43]
Semi-synthetic	Gum tragacanth	Lipase enzyme catalyzed biodegradable hydrogel-IPN system of GT with AAm and (MAA).	Composting method	77 days	100% (completely decomposed)	[45]
			Burial method		81.26% decomposed	
Semi-synthetic	Starch	Super absorbent hydrogel (SAH) of starch-modified poly (acrylic acid)				[46]
		SAH-1 (more starch)	Broth culture method	6 weeks	~ 57%	
		SAH-2			~ 55%	
		SAH-3 (less starch)			~ 35%	
		PAA			~ 10%	
		SAH-1 (more starch)	Burial method	3 months	40%	
		SAH-2			33%	
		SAH-3 (less starch)			28%	
		PAA			5%	
Natural-modified	Cellulose	All NaCMC hydrogels	Immersion method at 30 °C	33-38 days	100% (completely decomposed)	[12]
		NaCMC-1 hydrogel (lower gel formation and crosslinker amount)		33 days		
		NaCMC-4 hydrogel (higher gel formation and crosslinker amount)		38 days		
Semi-synthetic	Chitosan	Chitosan/polyacrylic acid /copper hydrogel nanocomposites (CS/PAA/Cu-HNCs)	Immersion method	24 h		[49]
		CS-NPs-Cu 0%, 1%, 2% 3%			50% / 40% / 33% / 28%	
		CS/PAA/Cu-HNCs 0%, 1%, 2%, 3%			30% / 25% / 20% / 10%	
Semi-synthetic	From Coco peat	SRFH [CP-g-P(AAc)/NPK] hydrogel	Burial method	2 weeks / 12 weeks	0% / 100% completely decomposed	[56]
		CSAP			0% / 0%	
Semi-synthetic	Starch	Starch-g-poly (AA-co-AAm)/NCNps/Urea superabsorbent polymer SRF8	Burial method	30 days	17.3 %	[59]
		Starch-g-poly (AA-co-AAm)/NCNps/Urea superabsorbent polymer SRF10			23.9 %	

CHAPTER 4: CONCLUSIONS

In this review, a comprehensive coverage of the recent progress on polysaccharides-based hydrogels has been presented, from the perspective of fundamental investigation, delivery system, swelling, water-retention, water-holding, biodegradability, and other factors that can affect their performance. This provides an overview of the advantages, properties, evaluation methods, and factors that influence the performance of these materials, which I expect facilitates and serves as a guide for the development and implementation of them.

Polysaccharide-based hydrogels have proven to be an excellent option in the field of agriculture since their implementation generates several advantages from an economic and environmental point of view. It is very important to know the properties of these materials since the performance of the hydrogel will depend on these. Knowing the properties of hydrogels lets to know in what type of soil and crop they will have better performance since as it was exposed before, the effective application of hydrogels will depend on environmental factors, the medium in which they are applied, the synthesis methods used as well as the reagents and materials involved in the formation of the material. Recognizing the properties of hydrogels allows us to know their scope and effectiveness in agricultural production.

Swelling is a property that allows measuring the storage capacity of the hydrogel, which allows better control of resources, since depending on the swelling capacity, the material may be able to store a higher or lower amount of water and nutrients, avoiding the waste of resources and reducing the constant application of them, to the soils. Water holding and water retention are properties that let analyze the capacity of the matrix to maintain the water inside the hydrogel, this allows to have an idea of the time that the material will be able to store water and nutrients, and thus know the approximate time that the needs of the crops will be covered.

Slow-release is one of the main properties of hydrogels, since it allows the release of nutrients and water progressively to the crops, and better manages the resources, in order to reduce the negative effects on the environment, caused by the instant release of nutrients.

Finally, biodegradability is a property of great relevance, mainly in agriculture, since the effectiveness of the material is not only related to the advantages in agricultural production, in addition to this, a material used in the agricultural field must guarantee environmental care. Hydrogels formed by polysaccharides enable this option since they allow to improve and increase the agricultural production, and at the same time take care of the environment, since they degrade and do not produce secondary effects on soils, which reduces the probability of future environmental problems. A hydrogel that presents these properties is of great value since it reduces the environmental impact and favors the quality and production of the crops.

CHAPTER 5: PERSPECTIVES

During the last years the use of superabsorbents for controlled release of fertilizers, have been positioned in the market since they present excellent characteristics that benefit the agricultural production, since have high absorption and retention of water, and help to control the release of nutrients in the soil, which reduces the environmental impact and improves the quantity and quality of crops. In addition, they are materials that help to increase agricultural production, helping to solve the problem of high food demand, caused by the constant growth of the population.

At a global level, agriculture is one of the fundamental fields since the feeding of the population depends on it. In countries like Ecuador, food production is one of the main sources of the country´s economy, because many of the produced crops are exported to other countries. Therefore, the country can benefit from improvements in agriculture such as those mentioned above.

Controlled nutrient release formulations help to care of the soils, improve production, and reduce pollution. It is of great importance to spread the benefits of these materials, in order to be used in the country's agriculture. In addition, as superabsorbents are based on polysaccharides, there is a wide availability of raw material to develop them, since in Ecuador a high amount of food waste and crop residues are generated. In this way the soils and the environment can benefit, since the impact produced by common fertilizers is reduced. Consequently, the crop and food residues are recycled acquiring an added value by hydrogels obtaining based on those residues, instead of being burnt or simply accumulated, since the elimination of them is difficult because of their excessive quantity.

With these reflections in mind, there is a great potential of polysaccharide-hydrogels as controlled-release systems of fertilizers to grow and succeed. This would require close collaboration between the designers and end-users to identify the agricultural needs yet not addressed by the existing hydrogels and to establish appropriate design priorities and criteria.

Bibliography

1. Campos EVR, de Oliveira JL, Fraceto LF, Singh B. Polysaccharides as safer release systems for agrochemicals. Agron Sustain Dev [Internet] 2015;35(1):47–66. Available from: http://link.springer.com/10.1007/s13593-014-0263-0
2. FAO. 2050: A third more mouths to feed. Food Agric Organ United Nations [Internet] 2009;(October):1–5. Available from: http://www.fao.org/news/story/en/item/35571/icode/
3. Soby SD. The End of the Green Revolution. J Agric Environ Ethics [Internet] 2013;26(3):537–46. Available from: http://link.springer.com/10.1007/s10806-012-9393-z
4. Sinha D, Tandon PK. An Overview of Nitrogen, Phosphorus and Potassium: Key Players of Nutrition Process in Plants [Internet]. In: Sustainable Solutions for Elemental Deficiency and Excess in Crop Plants. Singapore: Springer Singapore; 2020. page 85–117.Available from: https://link.springer.com/10.1007/978-981-15-8636-1_5
5. Gupta K, Bordoloi N, Baruah KK, Gorh D. Role of Starch Polymer-Coated Urea in the Mitigation of Greenhouse Gas Emissions from Rice and Wheat Ecosystems [Internet]. In: Ecological and Practical Applications for Sustainable Agriculture. Singapore: Springer Singapore; 2020. page 131–48.Available from: http://link.springer.com/10.1007/978-981-15-3372-3_7
6. Savci S. An Agricultural Pollutant: Chemical Fertilizer. Int J Environ Sci Dev [Internet] 2012;3(1):73–80. Available from: http://www.ijesd.org/show-35-736-1.html
7. Ramli RA. Slow release fertilizer hydrogels: a review. Polym Chem [Internet] 2019;10(45):6073–90. Available from: http://xlink.rsc.org/?DOI=C9PY01036J
8. Llanes L, Dubessay P, Pierre G, Delattre C, Michaud P. Biosourced Polysaccharide-Based Superabsorbents. Polysaccharides [Internet] 2020;1(1):51–

79. Available from: https://www.mdpi.com/2673-4176/1/1/5

9. Jones Jr. JB. Plant Nutrition and Soil Fertility Manual [Internet]. CRC Press; 2012. Available from: https://www.taylorfrancis.com/books/9781439816103

10. Matthews JA. Soil texture [Internet]. In: Encyclopedia of Environmental Change. 2455 Teller Road, Thousand Oaks, California 91320: SAGE Publications, Ltd.; 2014. page 5.Available from: http://sk.sagepub.com/reference/dictionaryenvirochange/n3624.i1.xml

11. Kirkby E. Introduction, Definition and Classification of Nutrients [Internet]. In: Marschner's Mineral Nutrition of Higher Plants. Elsevier; 2012. page 3–5.Available from: https://linkinghub.elsevier.com/retrieve/pii/B9780123849052000017

12. Akalin, Gulen Oytun; Pulat M, Akalin GO, Pulat M. Preparation of Sodium Carboxymethly Cellulose Hydrogels for Controlled Release of Copper Micronutrient. Technol Eng Math [Internet] 2018;2(2):25–34. Available from: www.isres.org

13. Welch RM, Shuman L. Micronutrient Nutrition of Plants. CRC Crit Rev Plant Sci [Internet] 1995;14(1):49–82. Available from: https://www.tandfonline.com/doi/full/10.1080/07352689509701922

14. Akalin GO, Pulat M. Controlled release behavior of zinc-loaded carboxymethyl cellulose and carrageenan hydrogels and their effects on wheatgrass growth. J Polym Res [Internet] 2020;27(1):6. Available from: http://link.springer.com/10.1007/s10965-019-1950-y

15. Vudjung C, Saengsuwan S. Biodegradable IPN Hydrogels Based on Pre-vulcanized Natural Rubber and Cassava Starch as Coating Membrane for Environment-Friendly Slow-Release Urea Fertilizer. J Polym Environ [Internet] 2018;26(9):3967–80. Available from: http://link.springer.com/10.1007/s10924-018-1274-8

16. Sam ST, Nuradibah MA, Ismail H, Noriman NZ, Ragunathan S. Recent Advances in Polyolefins/Natural Polymer Blends Used for Packaging Application. Polym Plast Technol Eng [Internet] 2014;53(6):631–44. Available from: http://www.tandfonline.com/doi/abs/10.1080/03602559.2013.866247

17. Liu Z, Jiao Y, Wang Y, Zhou C, Zhang Z. Polysaccharides-based nanoparticles as drug delivery systems. Adv Drug Deliv Rev [Internet] 2008;60(15):1650–62. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0169409X08002287

18. BeMiller JN. Polysaccharides [Internet]. In: Carbohydrate Chemistry for Food Scientists. Elsevier; 2019. page 103–57.Available from: https://doi.org/10.1016/B978-0-12-812069-9.00005-4

19. Abdul Khalil HPS, Chong EWN, Owolabi FAT, Asniza M, Tye YY, Rizal S, et al. Enhancement of basic properties of polysaccharide-based composites with organic and inorganic fillers: A review. J Appl Polym Sci [Internet] 2019;136(12):47251. Available from: https://onlinelibrary.wiley.com/doi/10.1002/app.47251

20. OLIVEIRA JT, REIS RL. Hydrogels from polysaccharide-based materials: Fundamentals and applications in regenerative medicine [Internet]. In: Natural-Based Polymers for Biomedical Applications. Elsevier; 2008. page 485–514.Available from: https://doi.org/10.1533/9781845694814.4.485

21. Okay O. General Properties of Hydrogels [Internet]. 2009. page 1–14.Available from: https://doi.org/10.1007/978-3-540-75645-3_1

22. Qureshi MA, Nishat N, Jadoun S, Ansari MZ. Polysaccharide based superabsorbent hydrogels and their methods of synthesis: A review. Carbohydr Polym Technol Appl [Internet] 2020;1(November):100014. Available from: https://doi.org/10.1016/j.carpta.2020.100014

23. Kalia S, Sabaa MW. Polysaccharide Based Graft Copolymers [Internet]. Berlin, Heidelberg: Springer Berlin Heidelberg; 2013. Available from: http://dx.doi.org/10.1007/978-3-642-36566-9

24. Qiao D, Liu H, Yu L, Bao X, Simon GP, Petinakis E, et al. Preparation and characterization of slow-release fertilizer encapsulated by starch-based superabsorbent polymer. Carbohydr Polym [Internet] 2016;147:146–54. Available from: http://dx.doi.org/10.1016/j.carbpol.2016.04.010

25. Mohammed Soliman F, Yang W, Guo H, Ibrahim Shinger M, Mahmoud Idris A, Suliman Hassan E. Preparation of Carboxymethyl Cellulose-g-Poly (Acrylic Acid-2-Acrylamido-2-Methylpropane Sulfonic Acid)/Attapulgite Superabsorbent Composite Preparation of Carboxymethyl Cellulose-g-Poly (Acrylic Acid-2-

Acrylamido-2-Methylpropane Sulfonic Acid)/Attapulgit. Compos Am J Polym Sci Technol [Internet] 2016;2(1):11–9. Available from: http://www.sciencepublishinggroup.com/j/ajpst

26. Olad A, Zebhi H, Salari D, Mirmohseni A, Reyhani Tabar A. Slow-release NPK fertilizer encapsulated by carboxymethyl cellulose-based nanocomposite with the function of water retention in soil. Mater Sci Eng C [Internet] 2018;90(April):333–40. Available from: https://doi.org/10.1016/j.msec.2018.04.083

27. De Guzman J, Dela Peña K, Ytac Dorothy J, Tumolva T. Synthesis and Characterization of Ionically-Crosslinked *κ*- Carrageenan/Sodium Alginate/Carboxymethyl Cellulose Hydrogel Blends for Soil Water Retention and Fertilizer Release. Solid State Phenom [Internet] 2020;304:59–65. Available from: https://www.scientific.net/SSP.304.59

28. Elbarbary AM, Ghobashy MM. Controlled release fertilizers using superabsorbent hydrogel prepared by gamma radiation. Radiochim Acta [Internet] 2017;105(10):865–76. Available from: https://www.degruyter.com/document/doi/10.1515/ract-2016-2679/html

29. Yanmin Shen, He Wang, Zijun Liu, Weikun Li, Yuhua Liu, Jingjing Li, Hongliang Wei HH. Fabrication of a water-retaining, slow-release fertilizer based on nanocomposite double-network hydrogels via ion-crosslinking and free radical polymerization [Internet]. 2020. Available from: https://doi.org/10.1016/j.jtho.2021.03.017

30. Andani G, Helmiyati H. Synthesis and characterization of hydrogel NaCMC-g-poly(AA-co-AAm) modified by rice husk ash as macronutrient NPK slow-release fertilizer superabsorbent. IOP Conf Ser Mater Sci Eng [Internet] 2020;763(1):012005. Available from: https://iopscience.iop.org/article/10.1088/1757-899X/763/1/012005

31. Funami T, Hiroe M, Noda S, Asai I, Ikeda S, Nishinari K. Influence of molecular structure imaged with atomic force microscopy on the rheological behavior of carrageenan aqueous systems in the presence or absence of cations. Food Hydrocoll [Internet] 2007;21(4):617–29. Available from: https://doi.org/10.1016/j.foodhyd.2006.07.013

32. Narayanan A, Dhamodharan R. Super water-absorbing new material from chitosan, EDTA and urea. Carbohydr Polym [Internet] 2015;134:337–43. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0144861715007511

33. Sabadini RC, Martins VCA, Pawlicka A. Synthesis and characterization of gellan gum: chitosan biohydrogels for soil humidity control and fertilizer release. Cellulose [Internet] 2015;22(3):2045–54. Available from: http://dx.doi.org/10.1007/s10570-015-0590-6

34. Mohammadi-Khoo S, Moghadam PN, Fareghi AR, Movagharnezhad N. Synthesis of a cellulose-based hydrogel network: Characterization and study of urea fertilizer slow release. J Appl Polym Sci [Internet] 2016;133(5):n/a-n/a. Available from: https://doi.org/10.1002/app.42935

35. Feng D, Bai B, Wang H, Suo Y. Enhanced mechanical stability and sensitive swelling performance of chitosan/yeast hybrid hydrogel beads. New J Chem [Internet] 2016;40(4):3350–62. Available from: http://xlink.rsc.org/?DOI=C5NJ02404H

36. Senna AM, Braga Do Carmo J, Santana Da Silva JM, Botaro VR. Synthesis, characterization and application of hydrogel derived from cellulose acetate as a substrate for slow-release NPK fertilizer and water retention in soil. J Environ Chem Eng [Internet] 2015;3(2):996–1002. Available from: http://dx.doi.org/10.1016/j.jece.2015.03.008

37. Zhang H, Luan Q, Huang Q, Tang H, Huang F, Li W, et al. A facile and efficient strategy for the fabrication of porous linseed gum/cellulose superabsorbent hydrogels for water conservation. Carbohydr Polym [Internet] 2016;157:1830–6. Available from: http://dx.doi.org/10.1016/j.carbpol.2016.11.070

38. Li X, Li Q, Xu X, Su Y, Yue Q, Gao B. Characterization, swelling and slow-release properties of a new controlled release fertilizer based on wheat straw cellulose hydrogel. J Taiwan Inst Chem Eng [Internet] 2016;60:564–72. Available from: https://doi.org/10.1016/j.jtice.2015.10.027

39. Essawy HA, Ghazy MBM, El-Hai FA, Mohamed MF. Superabsorbent hydrogels via graft polymerization of acrylic acid from chitosan-cellulose hybrid and their potential in controlled release of soil nutrients. Int J Biol Macromol [Internet]

2016;89:144–51. Available from: http://dx.doi.org/10.1016/j.ijbiomac.2016.04.071

40. Xiao X, Yu L, Xie F, Bao X, Liu H, Ji Z, et al. One-step method to prepare starch-based superabsorbent polymer for slow release of fertilizer. Chem Eng J [Internet] 2016;309:607–16. Available from: http://dx.doi.org/10.1016/j.cej.2016.10.101

41. Narayanan A, Kartik R, Sangeetha E, Dhamodharan R. Super water absorbing polymeric gel from chitosan, citric acid and urea: Synthesis and mechanism of water absorption. Carbohydr Polym [Internet] 2018;191(2505):152–60. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0144861718302844

42. Calcagnile P, Sibillano T, Giannini C, Sannino A, Demitri C. Biodegradable poly(lactic acid)/cellulose-based superabsorbent hydrogel composite material as water and fertilizer reservoir in agricultural applications. J Appl Polym Sci [Internet] 2019;136(21):47546. Available from: https://onlinelibrary.wiley.com/doi/10.1002/app.47546

43. Akalin GO, Pulat M. Preparation and characterization of κ-carrageenan hydrogel for controlled release of copper and manganese micronutrients. Polym Bull [Internet] 2020;77(3):1359–75. Available from: http://link.springer.com/10.1007/s00289-019-02800-4

44. Rozo G, Bohorques L, Santamaría J. Controlled release fertilizer encapsulated by a κ-carrageenan hydrogel. Polímeros [Internet] 2019;29(3):2–8. Available from: http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0104-14282019000300403&tlng=en

45. Saruchi, Kumar V, Mittal H, Alhassan SM. Biodegradable hydrogels of tragacanth gum polysaccharide to improve water retention capacity of soil and environment-friendly controlled release of agrochemicals. Int J Biol Macromol [Internet] 2019;132:1252–61. Available from: https://doi.org/10.1016/j.ijbiomac.2019.04.023

46. Sarmah D, Karak N. Biodegradable superabsorbent hydrogel for water holding in soil and controlled-release fertilizer. J Appl Polym Sci [Internet] 2020;137(13):48495. Available from: https://doi.org/10.1002/app.48495

47. Hendrawan, Khoerunnisa F, Sonjaya Y, Chotimah N. Physical and chemical

characteristics of alginate-poly (vinyl alcohol) based controlled release hydrogel. J Environ Chem Eng [Internet] 2016;4(4):4863–9. Available from: http://dx.doi.org/10.1016/j.jece.2016.03.043

48. León O, Muñoz-Bonilla A, Soto D, Ramirez J, Marquez Y, Colina M, et al. Preparation of Oxidized and Grafted Chitosan Superabsorbents for Urea Delivery. J Polym Environ [Internet] 2018;26(2):728–39. Available from: https://doi.org/10.1007/s10924-017-0981-x

49. Abd El-Aziz ME, Morsi SMM, Salama DM, Abdel-Aziz MS, Abd Elwahed MS, Shaaban EA, et al. Preparation and characterization of chitosan/polyacrylic acid/copper nanocomposites and their impact on onion production. Int J Biol Macromol [Internet] 2019;123:856–65. Available from: https://doi.org/10.1016/j.ijbiomac.2018.11.155

50. Pan X, Zhuang X-W, Chen S-W. Rice Husk Char/Poly-(Acrylic Acid-co-acrylamide) Superabsorbent Hydrogels: Preparation, Characterization, and Swelling Behaviors. BioResources [Internet] 2017;12(3):4795–809. Available from: http://ojs.cnr.ncsu.edu/index.php/BioRes/article/view/11372

51. Zhou T, Wang Y, Huang S, Zhao Y. Synthesis composite hydrogels from inorganic-organic hybrids based on leftover rice for environment-friendly controlled-release urea fertilizers. Sci Total Environ [Internet] 2018;615:422–30. Available from: https://doi.org/10.1016/j.scitotenv.2017.09.084

52. Stanley N, Mahanty B. Preparation and characterization of biogenic CaCO3-reinforced polyvinyl alcohol–alginate hydrogel as controlled-release urea formulation. Polym Bull [Internet] 2019;(0123456789). Available from: https://doi.org/10.1007/s00289-019-02763-6

53. León O, Soto D, González J, Piña C, Muñoz-Bonilla A, Fernandez-García M. Environmentally Friendly Fertilizers Based on Starch Superabsorbents. Materials (Basel) [Internet] 2019;12(21):3493. Available from: https://www.mdpi.com/1996-1944/12/21/3493

54. Iftime MM, Ailiesei GL, Ungureanu E, Marin L. Designing chitosan based eco-friendly multifunctional soil conditioner systems with urea controlled release and water retention. Carbohydr Polym [Internet] 2019;223(July):115040. Available

from: https://doi.org/10.1016/j.carbpol.2019.115040

55. de Souza AG, Cesco CT, de Lima GF, Artifon SES, Rosa D dos S, Paulino AT. Arabic gum-based composite hydrogels reinforced with eucalyptus and pinus residues for controlled phosphorus release. Int J Biol Macromol [Internet] 2019;140:33–42. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0141813019345386

56. Ramli RA, Lian YM, Nor NM, Azman NIZ. Synthesis, characterization, and morphology study of coco peat-grafted-poly(acrylic acid)/NPK slow release fertilizer hydrogel. J Polym Res [Internet] 2019;26(12):266. Available from: http://link.springer.com/10.1007/s10965-019-1952-9

57. Zhang X, Liu Y, Lu P, Zhang M. Preparation and properties of hydrogel based on sawdust cellulose for environmentally friendly slow release fertilizers. Green Process Synth [Internet] 2020;9(1):139–52. Available from: https://www.degruyter.com/document/doi/10.1515/gps-2020-0015/html

58. Lohmousavi SM, Abad HHS, Noormohammadi G, Delkhosh B. Synthesis and characterization of a novel controlled release nitrogen-phosphorus fertilizer hybrid nanocomposite based on banana peel cellulose and layered double hydroxides nanosheets. Arab J Chem [Internet] 2020;13(9):6977–85. Available from: https://doi.org/10.1016/j.arabjc.2020.06.042

59. Salimi M, Motamedi E, Motesharezedeh B, Hosseini HM, Alikhani HA. Starch-g-poly(acrylic acid-co-acrylamide) composites reinforced with natural char nanoparticles toward environmentally benign slow-release urea fertilizers. J Environ Chem Eng [Internet] 2020;8(3):103765. Available from: https://linkinghub.elsevier.com/retrieve/pii/S2213343720301135

60. Sasmal PK, Patra S. Effect in Growth of Corn Plant from Cellulose-Based Hydrogel Derived from Wheat Straw. J Inst Eng Ser E [Internet] 2020;1–6. Available from: https://link.springer.com/10.1007/s40034-020-00180-3

61. Wang W, Yang Z, Zhang A, Yang S. Water retention and fertilizer slow release integrated superabsorbent synthesized from millet straw and applied in agriculture. Ind Crops Prod [Internet] 2020;160(November):113126. Available from: https://doi.org/10.1016/j.indcrop.2020.113126

62. Pushpamalar J, Langford SJ, Ahmad MB, Lim YY, Hashim K. Eco-friendly smart hydrogels for soil conditioning and sustain release fertilizer. Int J Environ Sci Technol [Internet] 2018;15(10):2059–74. Available from: http://link.springer.com/10.1007/s13762-017-1598-2

63. Zonatto F, Muniz EC, Tambourgi EB, Paulino AT. Adsorption and controlled release of potassium, phosphate and ammonia from modified Arabic gum-based hydrogel. Int J Biol Macromol [Internet] 2017;105:363–9. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0141813017312436

64. Rodrigues Sousa H, Lima IS, Neris LML, Silva AS, Santos Nascimento AMS, Araújo FP, et al. Superabsorbent Hydrogels Based to Polyacrylamide/Cashew Tree Gum for the Controlled Release of Water and Plant Nutrients. Molecules [Internet] 2021;26(9):2680. Available from: https://www.mdpi.com/1420-3049/26/9/2680

65. Singh J, Dhaliwal AS. Water retention and controlled release of KCl by using microwave-assisted green synthesis of xanthan gum-cl-poly (acrylic acid)/AgNPs hydrogel nanocomposite. Polym Bull [Internet] 2020;77(9):4867–93. Available from: http://link.springer.com/10.1007/s00289-019-02990-x

66. Olad A, Gharekhani H, Mirmohseni A, Bybordi A. Synthesis, characterization, and fertilizer release study of the salt and pH-sensitive NaAlg-g-poly(AA-co-AAm)/RHA superabsorbent nanocomposite. Polym Bull [Internet] 2017;74(8):3353–77. Available from: http://link.springer.com/10.1007/s00289-016-1899-5

67. Ehrenhofer A, Elstner M, Wallmersperger T. Normalization of hydrogel swelling behavior for sensoric and actuatoric applications. Sensors Actuators B Chem [Internet] 2018;255:1343–53. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0925400517315447

68. Dave PN, Gor A. Natural polysaccharide-based hydrogels and nanomaterials: Recent trends and their applications [Internet]. Elsevier Inc.; 2018. Available from: http://dx.doi.org/10.1016/B978-0-12-813351-4.00003-1

69. Guilherme MR, Aouada FA, Fajardo AR, Martins AF, Paulino AT, Davi MFT, et al. Superabsorbent hydrogels based on polysaccharides for application in agriculture as soil conditioner and nutrient carrier: A review. Eur Polym J [Internet]

2015;72:365–85. Available from: http://dx.doi.org/10.1016/j.eurpolymj.2015.04.017

70. USDA. Irrigation Water Management: Chapter 9. Irrig Guid [Internet] 2005;230. Available from: http://www.nespal.org/sirp/AWP/SCReport/NEH_Part_652_Chapter_09_Irrigation_Water_Management.pdf

71. Demitri C, Scalera F, Madaghiele M, Sannino A, Maffezzoli A. Potential of Cellulose-Based Superabsorbent Hydrogels as Water Reservoir in Agriculture. Int J Polym Sci [Internet] 2013;2013:1–6. Available from: http://www.hindawi.com/journals/ijps/2013/435073/

72. Lin P, Liu L, He G, Zhang T, Yang M, Cai J, et al. Preparation and properties of carboxymethyl chitosan/oxidized hydroxyethyl cellulose hydrogel. Int J Biol Macromol [Internet] 2020;162:1692–8. Available from: https://doi.org/10.1016/j.ijbiomac.2020.07.282

73. Fu J, Wang C, Chen X, Huang Z, Chen D. Classification research and types of slow controlled release fertilizers (SRFs) used - a review. Commun Soil Sci Plant Anal [Internet] 2018;49(17):2219–30. Available from: https://doi.org/10.1080/00103624.2018.1499757

74. Lawrencia D, Wong SK, Low DYS, Goh BH, Goh JK, Ruktanonchai UR, et al. Controlled Release Fertilizers: A Review on Coating Materials and Mechanism of Release. Plants [Internet] 2021;10(2):238. Available from: https://www.mdpi.com/2223-7747/10/2/238

75. Naz MY, Sulaiman SA. Slow release coating remedy for nitrogen loss from conventional urea: A review. J Control Release [Internet] 2016;225:109–20. Available from: http://dx.doi.org/10.1016/j.jconrel.2016.01.037

76. Hu S. Composting [Internet]. NRDC2020 [cited 2021 Oct 9];1–24. Available from: https://www.nrdc.org/stories/composting-101

77. Lahuerta Zamora L, Pérez-Gracia MT. Using digital photography to implement the McFarland method. J R Soc Interface [Internet] 2012;9(73):1892–7. Available from: https://royalsocietypublishing.org/doi/10.1098/rsif.2011.0809

78. Lozano GE, Beatriz SR, Cervantes FM, María GNP, Francisco JMC. Low accuracy of the McFarland method for estimation of bacterial populations. African J Microbiol Res [Internet] 2018;12(31):736–40. Available from: http://academicjournals.org/journal/AJMR/article-abstract/B84886158328