Natural fibers for hydrogels production and their applications in agriculture

Fibras naturales para la elaboración de hidrogeles y sus aplicaciones en la agricultura

Liliana Serna Cock[1] and Marcelo Alexander Guancha-Chalapud[2]

[1]Facultad de Ingeniería y Administración. Universidad Nacional de Colombia Sede Palmira, Colombia. Author for correspondence: lserna@unal.edu.co. [2]Centro Nacional de Asistencia Técnica a la Industria (ASTIN). Servicio Nacional deAprendizaje - SENA. Cali-Valle, Colombia Author for correspondence:lserna@unal.edu.co

Abstract

This paper presents a review on hydrogels applied to agriculture emphasizing on the use of natural fibers. The objectives were to examine, trends in research addressed to identify natural fibers used in hydrogels development and methods for modifying natural fibers, understand factors which determine the water retention capacity of a hydrogel. Consequently, this paper shows some methodologies used to evaluate the hydrogels efficiency and to collect in tables, relevant information in relation to methods of natural fibers modification and hydrogel synthesis. It was found that previous research focused on hydrogels development processed with biodegradable polymers such as starch, chitosan and modified natural fibers, cross-linked with potassium acrylate and acrylamide, respectively. In addition, current researches aimed to obtaining hydrogels with improved properties, which have allowed a resistance to climatic variations and soil physicochemical changes, such as pH, presence of salts, temperature and composition. In fact, natural fibers such as sugarcane, agave fiber and kapok fiber, modified with maleic anhydride, are an alternative to obtain hydrogels due to an increasing of mechanical properties and chemically active sites. However, the use of natural nanofibers in hydrogels, has been a successful proposal to improve hydrogels mechanical and swelling properties, since they give to material an elasticity and rigidity properties. A hydrogel efficiency applied to soil, is measured throughout properties as swellability, mechanical strength, and soil water retention. It was concluded that hydrogels, are an alternative to the current needs for the agricultural sector.

Key words: Hydrogels, methods of modifying fiber, nanofibers, superabsorbent, water retention capacity.

Resumen

En el presente artículo se presenta una revisión de literatura sobre hidrogeles aplicados a la agricultura, haciéndose mayor énfasis en el uso de fibras vegetales. Los objetivos fueron examinar las tendencias en la investigación, identificar las fibras naturales utilizadas en el desarrollo de hidrogeles, mostrar los métodos de modificación de fibras naturales para la elaboración de hidrogeles, entender los factores que determinan la capacidad de retención de agua de un hidrogel, mostrar algunas metodologías empleadas para evaluar la eficiencia de un hidrogel y recopilar en tablas, información relevante en relación a métodos de modificación de fibras naturales y de síntesis de hidrogeles. Se encontró que las investigaciones se orientan al desarrollo de hidrogeles elaborados a bases de polímeros biodegradables como almidón, quitosano y fibras vegetales modificadas, entrecruzadas con acrilato de potasio y acrilamida. Además, las investigaciones apuntan a la obtención de hidrogeles con propiedades mejoradas, que permitan resistir las variaciones climáticas y los cambios fisicoquímicos del suelo como el pH, la presencia de sales, temperatura y composición. Fibras naturales como caña de azúcar, fibra de agave y fibra de kapoc, modificadas con anhídrido maléico, son una alternativa para la obtención de hidrogeles debido al incremento de las propiedades mecánicas, sumado al incremento de los sitios químicamente activos. Sin embargo, el uso de nanofibras naturales ha sido una propuesta exitosa para mejorar las propiedades mecánicas y de hinchamiento de los hidrogeles, ya que aportan al material elasticidad y rigidez. La eficiencia de un hidrogel aplicado al suelo se mide a través de propiedades como capacidad de hinchamiento resistencia mecánica y retención de agua en el suelo. Se concluyó que los hidrogeles, son una alternativa a las necesidades actuales del sector agrícola.

Palabras clave: Capacidad de retención de agua, hidrogeles, métodos de modificación de fibras, nanofibras, superabsorbentes.

Introduction

Population growth necessitates an increasing demand for agricultural products in quantity and diversity, which translates into a greater water demand for agricultural activities and a greater soil intensification use available for crops (FAO, 2013). In Colombia, agriculture consumes about 70% of available water (Arévalo, 2012; IDEAM, 2014; IDEAM, 2015). Hydrogels are presented as an alternative to the current needs for the agricultural sector due to most crops requires an additional irrigation. Hydrogels are polymers which have a three-dimensional cross-linked structure that allows them to absorb, store and release water molecules (Mohan, Murthy & Raju, 2006; Pourjavadi & Mahdavinia, 2006). Among the most important applications are as follows: manufacture of personal hygiene products, medical (Arredondo, 2009), environmental (heavy metals removal) (Orozco-Guareno, Hernandez, Gomez-Salazar, Mendizabal & Katime, 2011) and agriculture (Cortés *et al.*, 2007; Liang, Huang, Zhang, Hu & Liu, 2013). The most important agricultural areas are gardening, horticulture and silviculture, respectively (Journal the Business, 2015; Vundavalli, Vundavalli, Nakka & Rao, 2015). In Colombia, hydrogels application is addressed to counteract drought in crops such as mango in the municipality of Magangue-Bolivar, Colombia (Asohofrucol, 2014). In 2014, the superabsorbent hydrogels global production was 3119 million tons. An increase of 11.8% over the previous year. Among the countries with the highest demand for the product are as follows: China, Japan, United States, Germany and countries in the Middle East. Although most of this product is intended for hygiene products manufacture, the agricultural industry occupies the second place in superabsorbent hydrogels consumption (Cannazza, Cataldo, De Benedetto, Demitri, Madaghiele & Sannino, 2014).

Hydrogels for agricultural applications are based on synthesized acrylates. These components have allowed an increasing in the soil available water, which induce to fast growth (Gascue, Aguilera, Ramirez, Prin & Torres, 2006), prolong a plant survival under water stress (Cannazza *et al.*, 2014; Cortés *et al.*, 2007; Hüttermann, Orikiriza & Agaba, 2009; Mo, Shu-quan, Hua-min, Zhan-bin & Shu-qin, 2006; Zhong, Zheng, Mao, Lin & Jiang, 2012) and have allowed a controlled release of fertilizers (Liu *et al.*, 2013). One of the major limitations in hydrogels use for agricultural applications is the low mechanical resistance (Guilherme *et al.*, 2015; Sannino, Demitri & Madaghiele, 2009). A pressure exerted by the plant and soil layer on the hydrogel, influences the loss of swelling capacity, elasticity and rigidity, respectively (Feng, Li & Wang, 2010). To maintain a polymer elasticity, long chain molecules and a suitable crosslinking are required

to dissipate the mechanical energy, which is caused by the pressure exerted on the hydrogel (Sannino *et al.*, 2009). One of the alternatives to improve the mechanical properties is the use of natural fibers (Rodrigues *et al.*, 2013), these fibers are characterized by containing cellulose, hemicellulose and lignin, respectively (Bessadok, Marais, Roudesli, Lixon & Métayer, 2008)natural fibres are more and more considered as reinforcement in composite materials. In this work, to improve the adhesion between a polyester matrix (unsaturated polyester resin. The lignin layer which covers the cellulose of natural fibers and hinders the reaction with other molecules (Chang & Zhang, 2011). Given these concerns, is necessary to perform pretreatments and chemical modifications to improve the natural fibers reactivity (Feng *et al.*, 2010; Sannino *et al.*, 2009). It is important to note that most commercial hydrogels are based on non-biodegradable acrylic. Therefore, cellulose-based hydrogels fit well in the current trend to develop ecological alternatives addressed to hydrogels production (Sannino *et al.*, 2009). Given these concerns, the aim of this review was to present a research carried out on the methods of hydrogel synthesis based on natural fibers, the characterization methods and their evaluation during soil application. In addition, identify the research trends in this field.

Natural fibers for hydrogels production

Natural fibers are used as a reinforcement in composite materials as an alternative to replace the use of synthetic fibers in order to obtain low-cost and environmentally friendly products (Cuéllar & Muñoz, 2010; Kalia, Kaith & Kaur, 2014; Rodriguez, Jose, Daniel, Viviane & Alves Lavinia, 2014; Thakur & Thakur, 2014). Natural fibers are the most abundant polymers in nature, which are present in leaves, stems, seeds and plant fruits (Thomas, Paul, Pothan & Deepa, 2011). Some examples are flax fibers, jute, pitch, plantain, among others. These are characterized by their strength, flexibility, easy processing and biodegradability (Thakur & Thakur, 2014). The biodegradation rate of natural fibers depends on the environmental conditions and the degradation capacity of the microbial population (Malherbe & Cloete, 2002). Although specific bio-degradability data for natural fibers are not reported in the literature. The biodegradability method of natural fibers in composite materials is reported. For example, Sahoo, Sahu, Rana & Das, (2005), report the biodegradation of jute fiber and jute fiber crosslinked with polybutylacrylate using soil biodegradability method. In fact, the method is to bury a sample of known fiber weight or material to be studied at a specific soil depth under controlled conditions of humidity and temperature, and determine weight loss over time. The authors mentioned that during 12 months of evaluation, the fibers presented greater weight loss (47.1%) (greater

degradation) compared to the composite material (31.8%) (jute fibers cross-linked with polybuty-acrylate). On the other hand, Wu (2012), studied the polylactic acid biodegradability reinforced with stay fibers at concentrations between 20 and 40% by weight, using the soil bio-degradability method. He found greater weight loss in reinforced materials with higher stay fiber content during follow-up for six weeks. These fibers are characterized by mainly cellulose, hemicellulose and lignin, respectively (Bessadok *et al.*, 2008)natural fibres are more and

more considered as reinforcement in composite materials. In this work, to improve the adhesion between a polyester matrix (unsaturated polyester resin. Table 1, shows the composition and major mechanical properties of natural fibers. Cellulose is characterized by the presence of hydroxyl groups in the chain, which improve its reactivity, possibility of chemical modification, compatibility with other polymers and water solubility (Zhou, Fu, Zhang & Zhan, 2013).

Table 1. Composition in cellulose, hemicellulose and lignin (Abdul Khalil, Bhat, & Ireana Yusra, 2012) and mechanical properties of natural fibers (Pickering, Efendy & Le, 2015)

Natural Fiber	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extracts (%)	Density (g.cm^{-3})	Water absorption (%)*	Break resistance (%)	Tension resistance (MPa)	Module of Young (GPa)
Ramio	76	17	1	6	1.5	NR	2.0-3.8	400-938	400-128
Flax	63	12	3	13	1.5	NR	1.2-3.2	345-1830	27-80
Hemp	70	22	6	2	1.5	NR	1.6	550-1110	58-70
Jute	71	14	13	2	1.3-1.5	NR	1.5-1.8	393-800	10--55
Stay	73	14	11	2	1.3-1.6	56	2.0-2.5	507-855	9,4-28
Cotton	95	2	1	0,4	1.5-1.6	NR	1.5-2.4	188-308	18-28
Coconut	32-43	10—20	43—49	4	1.2	130-180	15-30	131-220	4-6

*Source: (Chandramohan & Marimuthu, 2011)

However, a lignin layer which coats the cellulose of natural fibers have achieved a difficulty to react with other molecules (Chang & Zhang, 2011). Given these concerns, is necessary to carry out pretreatments and chemical modifications to improve the reactivity and its interaction with other molecules (Feng *et al.*, 2010; Sannino *et al.*, 2009).

Modifying methods of natural fibers for hydrogels production

The modification methods of natural fibers usually are divided in two stages: a pretreatment, whose objective is the lignin removal throughout mechanical or chemical treatments by alkaline treatment (Shi, Wang, Zheng & Wang, 2014) and chemical modification, consisting of molecules insertion into the active sites (hydroxyl groups) of cellulose (Thomas *et al.*, 2011). These modifications increase the water absorption and retention capacity throughout an interaction with modifying agents and active sites generation (Liang *et al.*, 2013; R. F. Rodrigues, Trevenzoli, Santos, Leão & Botaro, 2006)avaliou-se a capacidade da madeira Paraju (Manilkara longifolia. Table 2, shows modifying agents used for different natural fibers, pretreatment conditions and the most significant effect.

Modification of sugarcane bagasse fibers using maleic anhydride, acetic anhydride, acrylic acid and styrene, increases the fibers hydrophobic capacity and decreasing mechanical tensile properties. Similarly, as indicated in Table 1,

agave fibers modified with maleic anhydrous and styrene showed an increasing tensile strength forces (Bessadok *et al.*, 2008). Therefore, modified fibers with maleic anhydride are an alternative for obtaining hydrogels due to an increasing in mechanical properties, which have allowed an increasing in chemical active sites of a modified chain due to a double link site, which allows a maleic anhydride adhesion to cellulose chain. Mechanical modification of plant fibers is another way of increasing the degree of gel swelling. In fact, the mechanical activation affects the destruction of a molecular lignin structure and an increasing of active sites in the cellulose throughout destruction of its crystalline structure (Huang *et al.*, 2009; Liang *et al.*, 2013). Similarly, Liang *et al.* (2013), found that increasing the mechanical modification time, increases the degree of swelling of a synthesized hydrogel from sugar cane bagasse and acrylic acid.

Nevertheless, the chemical modification methods for natural fibers present disadvantages as reactive use at high concentrations and high amount of solvent to carry out the reaction. In addition, reaction times are high, generally times vary between 1, 3, 24 and 48 hours. The number of stages is increased due to a separation, washing and neutralization operations involved with the used corrosive reagents nature and the amount of generated waste water (Chen et al., 2011; Liu et al., 2007). Therefore, other methods have been proposed to minimize the use of solvents. Alternatives such as assisted microwave modification, which is characterized

by using short reaction times and less solvent. Lie et al., (2009), performed the optimization of assisted cellulose modification by microwave using acetic anhydride as modifying agent, during the reaction tests the temperature, time, radiation potency were varied and iodine (I2) was used as the catalyst. The substitution degree of cellulose hydroxyl groups was evaluated by finding that substitution is increased with an increasing concentration of the catalyst. In this sense, modification were carried out using ultrasound, which becomes as a strategy to reduce the use of solvents and lignin removal. Ultrasonic pretreatment increased the lignin removal from sugarcane bagasse, which translates into a greater exposure of the cellulose hydroxyl groups, which may react with the modifying agent (Liu et al., 2007).

Table 2. Modifying methods of natural fibers for hydrogel synthesis

Type of fiber	Treatment conditions	Modifying agent	Effect	Reference
Sugar cane Bagasse	Pretreatment: Pyridine as solvent in ultrasound at 30°C, treatment times: 0-35 minutes. Modifying: Maleic anhydride (1.5g to 5.5g), using toluene as solvent. Reactor: Ball with three mouths with reflux. Reaction time: 30 to 120 min. Reaction temperature: 85 to 105°C	Chemical modifying with maleic anhydride	Time pretreatment increasing by ultrasound, increased the substitution degree of the modifying agent.	Liu et al., (2007)
Agave fiber	Reflux modifying 10% by weight of maleic anhydride with respect to acetone fiber with solvent, acetone fibers ratio (1/20) Reaction time: 25 hours Reaction temperature: 50°C	Maleic anhydride	Tensile properties increasing for fibers treated with maleic anhydride and styrene.	Bessadok et al., (2008)
	Reflux modifying with acetic anhydride Reaction temperature: 100°C Reaction time: 3 hours	Acetic anhydride		
	Acrylic acid modifying 0.3 M Reaction temperature: 85°C Reaction time: 1 hour	Acrylic acid		
	Styrene modifying 0.3M Reaction temperature: 85°C Reaction time: 1 hour	Styrene		
Cellulose	Microwave assisted modification optimization Catalyst: Iodine (I2) between 1 and 15 (%mol I_2/AGU (Anhydroglucose units) Microwave power: 300 to 800W Treatment time: 5 and 40 minutes Treatment temperature:80-130°C	Microwave assisted modification with acetic anhydride	The degree of substitution was increased with increasing catalyst, temperature, and irradiation power	Lie et al., (2009)
Sugar cane Bagasse	Reactor: Ball of three mouths of 500ml with reflux. Reaction temperature: 60°C Reaction time: 48 hours	Chemical modification: chloropoxypropane, tetraethylenepentamine	Increased swelling capacity and higher rate of release.	Zhong et al., (2012)
Sugar cane Bagasse	Mechanical activation at different treatment times: 0, 0.5, 1.0 and 1.5 hours.	Mechanical modification with high energy mill	Increased swelling capacity of the hydrogel for longer mechanical activation time.	Liang et al., 2013
Kapoc fiber	Pretreatment with $NaClO_2$ at 1% pretreatment temperature: 70-80°C Time: 1hour	Does not apply	Increased swelling capacity and elastic modulus by increasing the fiber percentage	Shi et al., (2014)

Hydrogels synthesis from plant fibers and effect on swelling ability

In general, the methods of hydrogels synthesis are carried out by mass polymerization, solution and reverse suspension, using an initiator and a cross-linker. The hydrogels synthesis based on plant fibers usually uses the solution polymerization method. In Table 3, some methods of hydrogels synthesis based on natural fibers are presented.

In tests carried out by Shi et al. (2014), described in Table 3, it was found that an increasing in the amount of fiber during the hydrogels synthesis, increased the swelling ability and the elastic modulus. However, natural fiber had achieved an increasing above 10% from a decreasing gel formation due to the fiber is insoluble in water and the active sites are decreased due to the initiator inefficiency.

Table 3. Methods of hydrogels synthesis based on natural fibers

Raw material	Polymerization conditions	Method	Type of characterization	Reference
Modified sugar cane bagasse, sodium hydroxide, acrylic acid. Cross-linker: N, N- bisacrylamide methylene. Initiator: Ammonium persulfate and sodium sulfite.	Reactor: Beaker of 250ml. Reaction temperature: 60°C Reaction time: 3hours	Polymerization in solution	Swelling ability. Swelling kinetics. Swelling ability to pH change. Swelling ability in saline solutions (NaCl, $CaCl_2$). Effect of temperature change on swelling ability.	Liang et al., 2013 Huang et al., 2009
Flax fiber (shive) pretreated with NaOH sodium hydroxide, acrylic acid. Cross-linker: N, N – bisacrylamide methylene. Initiator: Potassium Persulfate	Reactor set to microwave with condensation system Nitrogen as inert gas Reaction temperature: 22 minutes Power of irradiation: 160W	Microwave assisted polymerization	Swelling ability. Swelling kinetics. Swelling ability to pH change. Swelling ability in saline solutions (NaCl, $CaCl_2$ and $FelCl_3$). Biodegradability	Feng, Li, & Wang, (2010)
Commercial nanocrystalline cellulose, acrylamide Crosslinker: N, N-methylene bisacrylamide Initiator: Sodium persulphate and sodium bisulphite	Concentration of nanocrystals: 1, 3, 5, 6, 7 and 9.3% weight. Reactor: 50ml flask with stirring. Nitrogen as inert gas. Temperature: 25°C Reaction time: 20 hours.	Polymerization by free radicals in solution	Rheology of the gelation process Swelling ability and kinetics. Measurement of compression properties.	(C. Zhou, Wu, Yue, & Zhang, 2011)
Chitosan nanofibers, acrylamide. Crosslinker: N, N-methylene bisacrylamide Initiator: potassium persulfate and sodium bisulfite.	Concentration of 1.5% nanofibers with the monomer Reactor: 20x60mm test tubes Nitrogen as inert gas. Temperature: 40°C Reaction time: 20 hours.	Polymerization by free radicals in solution	Measurement of rheological and compression properties. Swelling ability and kinetics.	(C. Zhou & Wu, 2011)
Modified sugar cane bagasse. Phosphoric rock Acrylic acid partially neutralizing with NaOH and NH_3. Initiator: Potassium persulfate Crosslinker: N, N -methylether bisacrylamide	500ml three-necked reactor equipped with reflux Reaction time: 3 hours Reaction temperature: 75°C	Polymerization in solution	Determination of NPK Release ratio (Phosphorus) Swelling ability	Zhong et al., (2012).
Wheat straw pretreated with 1M HNO_3 Acrylic acid neutralized with KOH and dimethyl diallyl ammonium chloride Acrylamide Initiator: Potassium persulfate and ceramic ammonium nitrate Crosslinker: NN methylenebisacrylamide Cotton cellulose nanofibers.	Three-mouth reactor equipped with reflux Reaction time: 5 hours Reaction temperature: 50°C	Polymerization in solution	Swelling ability and water retention Swelling kinetics Re-swelling ability Swelling to pH change and in saline solutions.	Li et al., (2012)
Chitosan Acrylic acid Initiator: Potassium persulfate Crosslinker: NN methylene bisacrylamide.	Three-mouth reactor with reflux Reaction time: 2 hours Reaction temperature: 70°C	Polymerization in solution	Swelling in saline solutions and to pH change	Spagnol et al., (2012)
Cotton nanofibers, acrylamide and potassium acrylate Crosslinker: N, N-methylene bisacrylamide. Initiator: potassium persulfate. Catalyst: N, N, N, N-tetramethyldiamine	Concentration of nanofibres. 1, 5, 10, and 20% by relative weight to monomers. Reactor: No report Nitrogen as inert gas. Temperature: Not reported. Reaction time: 15 hours.	Polymerization by free radicals in solution	Swelling ability and kinetics. Swelling ability in saline solutions. Water retention capacity. Evaluation of the pH effect on the swelling ability.	(Spagnol, Rodrigues, Neto, et al., 2012)based on poly(acrylamide-co-acrylate
Cotton nanofibers, cassava starch and sodium acrylate. Crosslinker: N, N-methylene bisacrylamide. Initiator: Potassium persulfate.	Crosslinking concentration: 1 to 3% by weight. Concentration of nanofibers: 5 to 20% by weight. Reactor: Three-necked flask equipped with reflux with n stirring Reaction temperature: 70°C. Reaction time: 3 hours.	Polymerization by free radicals in solution	Kinetics and speed of swelling. Swelling ability in saline solutions and to pH change. Mechanical properties (Young's Modulus).	(Spagnol, Rodrigues, Pereira, et al., 2012b)
Pretreated flax fiber waste. Acrylic acid Acrylamide Initiator: Ammonium persulfate Crosslinker: NN methylene bisacrylamide.	Flask with reflux Reaction time: 2 hours Reaction temperature: 70°C	Polymerization in solution	Swelling by pH change and saline solutions Water holding capacity in the soil Water retention by temperature change	Wu et al., (2012)

Raw material	Polymerization conditions	Method	Type of characterization	Reference
Carboxylated cellulose nanofibers. Carboxymethyl cellulose Acrylic acid Acrylamide Initiator: Ammonium persulfate Crosslinker: NN methylene bisacrylamide.	Three-necked flask with reflux Reaction time: 2 hours Reaction temperature: 70°C	Polymerization in solution	Swelling ability. Retention and release capacity. Swelling to pH change and saline solutions Water retention capacity by temperature change	Zhou et al., (2013)
Kapoc Fiber Sodium hydroxide, acrylic acid. Crosslinker: N, N-methylene bisacrylamide Initiator: Ammonium persulfate.	Reactor: 250ml equipped with mechanical agitation Nitrogen as inert gas Reaction temperature: 70°C Reaction time: 3 hours	Polymerization in solution	Elastic module. Swelling ability. Swelling ability to pH change. Swelling kinetics. Swelling ability in saline solutions (NaCl, $CaCl_2$ and $AlCl_3$).	Shi et al., (2014)
Polyethylene glycol diacrylate Chitosan nanofibers, Initiator: ammonium persulfate. Crosslinker: NNNN-Tetramethyl ethylenediamide.	Reaction temperature: environment Reaction time: 30 minutes	Not reported	Swelling ability. Retention and release capacity. Resistance to compression and rupture.	Nitta et al., (2015)
Commercial cellulose nanofibers, sodium acrylate poly (ethylene glycol) diacrylate Photoinitiator: 1-phenyl hydroxycyclohexyl ketone.	Concentration of nanofibers: 0 to 2% by weight. Reactor: Beaker Reaction time: 8 minutes.	Photopolimerization by UV at 365nm of wave-length to a power of 100W.	Swelling ability free and in saline solutions	(Wen et al., 2015)

In the study reported in Table 3, Liang *et al.* (2013), showed the swelling is modified by the effect of pH change, the presence of salts (NaCl and $CaCl_2$) and temperature. In acidic media, the presence of hydronium ions interacts with the hydroxyl groups of cellulose chain, generating a greater presence of hydrogen linking forces, increasing the chain cross-links and a decreasing in the absorption capacity. In basic media, the present cation, interacts with the carboxyl group of the polyacrylate and polyacrylamide chain, neutralizing the electrostatic attraction active sites, which causes a decreasing in the swelling ability at higher saline concentration. With reference to temperature, the swelling ability was increased at temperatures between 0 and 50°C, at higher temperatures, decreases due to the surface water had achieved a higher energy compared to the attraction energy exerted by the polymer chain on the molecule. Similar results were obtained in hydrogels from kapok fibers (Shi *et al.*, 2014).

Specifically in flax fiber, Feng *et al.* (2010), found a decreasing swelling ability in saline solutions at acid (1-4) and basic (10-14) pH. The material biodegradation in 52 days was 40% at 40°C and performed an increasing in microorganism attack, since the material porosity and temperature promote the activation thereof.

Zhong *et al.* (2012), found that phosphoric rock inclusion in the polymer matrix, have allowed an improvement in the swelling ability and the rate of water release. In addition, this compound becomes an alternative for fertilizers inclusion in the polymer network whose advantage is a controlled release in the soil.

Nanofibers in hydrogels

Hydrogels with high swelling ability are usually fragile due to the lack of energy dissipation mechanisms and an uneven distribution of cross-linking points (C. Zhou & Wu, 2011). However, the use of natural fibers at nanoscale, improves the hydrogel mechanical properties due to they act as matrix reinforcement (Aouada, de Moura, Orts & Mattoso, 2011; Guilherme *et al.*, 2015; Krishnan K, Jose, K. R & George, 2015; Missoum, Belgacem & Bras, 2013) without affecting the swelling ability (Rodrigues *et al.*, 2013). In fact, the nanofibers have allowed to improve the swelling ability due to the capacity of forming hydrogen bridges, elasticity and available natural fiber surface (Nitta *et al.*, 2015; Zhou *et al.*, 2013; Spagnol, Rodrigues, Pereira *et al.*, 2012)the XRD pattern indicated that the nanofibrils crystallinity was as high as 90%. A 2 4-1 fractional factorial design was employed to evaluate the effect of acrylic acid/chitosan molar ratio, crosslinker, initiator, and filler in the swelling capacity of hydrogel composites. By the analysis of variance (ANOVA. The presence of hydrophylic groups (hydroxyl groups - OH) in the nanofibers, facilitate a more precise liquids diffusion into the hydrogel matrix more efficient and faster. Therefore, have allowed an increasing in the swelling rate (Spagnol, Rodrigues, Pereira *et al.*, 2012a, 2012b)the XRD pattern indicated that the nanofibrils crystallinity was as high as 90%. A 2 4-1 fractional factorial design was employed

to evaluate the effect of acrylic acid/chitosan molar ratio, crosslinker, initiator, and filler in the swelling capacity of hydrogel composites. By the analysis of variance (ANOVA. Spanol, Rodrigues, Neto *et al.* (2012a), Spagnol & Rodrigues, (2012b), who synthesized hydrogels from cotton cellulose nanofibers. They found the swelling ability was increased with an increasing in nanofiber content. Conversely, the swellability decreased for concentrations greater than 10% by weight in nanofibers. Similar results found by Zhou *et al.* (2013), at concentrations greater than 5% by weight in cellulose nanofibers content. In fact, an excessive increasing in the nanofibers content, which have allowed an increasing in the physical crosslinking and nanofiber stacking in polymer material networks, in which the water molecules are stored and results in a decreasing swelling ability (Spagnol & Rodrigues, 2012b).

The addition of nanofibers in hydrogels increases the density of cross-linking points, which improves the resistance to fracture, flexural strength and compression (Kabiri, Omidian, Doroudiani & Zohuriaan, 2011). Also, they promote the formation of a porous morphology (Wen, Zhu, Gauthier & An, 2015), which improves biodegradability, thermal stability and water retention capacity due to temperature changes in the medium (Aouada *et al.*, 2011). The resistance to compression and the elastic modulus is increased by chitosan nanofibers addition in polyethylene glycol acrylate based on hydrogels compared to hydrogels without nanofibers addition (Nitta *et al.*, 2015). As indicated in Table 2, Zhou & Wu (2011), evaluated the addition of chitosan nanofibers in hydrogels from acrylamide. The resistance to compression was increased for hydrogels based on chitosan nanofibers. This increase was attributed to a good nanofibers dispersion in the matrix, and the nanofibers interfacial adhesion to polyacrylamide chain. However, there was a decreasing in swelling ability due to a low chitosan affinity with water and the presence of amino (-NH$_2$) functional groups, which increased the crosslinking points density in the matrix, due to possible reactions that could be presented with the cross-linker.

Characterization of hydrogels

Swelling ability

In hydrogels, the swelling mechanism occurs by the solvent diffusion towards the hydrogel polymeric networks due to the hydrophilic capacity of the present functional groups (Guilherme *et al.*, 2015). The process causes the expansion of the cross-linked chains, hence an increasing in mass and volume. In fact, the swelling ability is determined by the gravimetric method (Guilherme *et al.*, 2015) Initially, dry hydrogel (xerogel) is weighed and immersed into an excess of distilled water or solvent of interest. The amount of water absorbed is determined by weight difference (Cortés *et al.*, 2007; Orozco-Guareno *et al.*, 2011). Generally, the test is performed in different periods of time until the maximum swelling ability is achieved, which have allowed the swelling kinetics determination. The swelling ability depends on the degree of hydrogel crosslinking. For hydrogels applied to agriculture, is necessary to determine properties that simulate soil conditions (Agaba, Orikiriza, Obua, Kabasa & Worbes, 2011; Ekebafe, Ekebafe, Ogbeifun & Okieimen, 2011). pH, the presence of salts and soil temperature are the major factors that influence the swelling ability (Chang, Han & Zhang, 2009; Delgado-Pelayo, Gallardo-Guerrero & Hornero-Méndez, 2014; Ullah, Othman, Javed, Ahmad & Akil, 2015). The presence of salts, acidic or basic pH and temperatures above 50°C decrease the swelling ability (Guilherme *et al.*, 2015; Shi *et al.*, 2014; Ullah *et al.*, 2015).

Li *et al.* (2012), studied the retention and re-swelling ability of hydrogels based on wheat straw. Water retention was determined using hydrogel samples with their maximum swelling ability using distilled water and saline solutions (NaCl, CaCl$_2$, Na$_2$SO$_4$, MgCl$_2$) and water release was studied by immersing the swollen hydrogel in saline solutions (NaCl 0.9%). It should be taken into account that hydrogel re-swelling is determined by performing swelling and drying cycles to the sample.

Resistance to compression and elastic modulus

When a material is subjected to an increasing tension in a single direction, a rupture occurs due to an increasing in microscopic material defects, the maximum tension that resists the material when it arrives at the point of fracture, is denominated resistance to the compression (Dianney *et al.*, 2010). In this sense, the resistance to compression is determined by a vertical force on the hydrogel surface in its maximum state of swelling. Nevertheless, the applied pressure and material displacement resulting from the compression, determine the mechanical properties, these are calculated throughout a theoretical model (Ahearne, Yang & Liu, 2008). Mechanical properties such as elastic modulus and resistance to compression are of great interest due to hydrogels for agricultural applications are affected by an exerted pressure of the soil layer and the pressure of the plant root system on the material (Sannino *et al.*, 2009).

The hydrogel samples are brought to their maximum swellability, which are subjected to

a resistance to compression at a rate of 0.1N. min^{-1} in a DMA analyzer (mechanical dynamic analysis) where a deformation-tension curve is obtained (Chang *et al.*, 2009). However, the resistance to compression and the elongation is increased in hydrogels obtained from pineapple leaf fiber pretreated with NaOH and acrylamide using NN-methylene bisacrylamide as compared to hydrogels obtained with untreated fiber due to an increasing chemical treatment in the fiber surface area, which improves the interfacial fiber adhesion into the acrylamide. In addition, the increase of active sites facilitates the initiator and crosslinker action (Ghazali, Adrus & Jamaluddin, 2014).

The elastic modulus in hydrogels is related to a hydrogel ability to return to its original state even were subjected to a force (Guilherme *et al.*, 2015). Alternatively, Nitta *et al.* (2015), determined the elastic modulus of hydrogels based on chitosan nanofibers throughout resistance to compression test using a rheometer. Previously, Cortés *et al.* (2007), evaluated the swelling ability at different mechanical loads and determined the elastic modulus of hydrogels throughout an application of a mechanical load using a piston.

The elastic modulus is increased by the addition of cotton cellulose nanofibers from a concentration of 10% by weight in hydrogels synthesized from cassava starch and sodium acrylate (Spagnol *et al.*, 2012b). Similar results were found in hydrogels synthesized based on acrylamide reinforced with chitosan nanofibers. In fact, the results of the resistance to compression, indicates an increasing (50.2KPa) measurement, compared to hydrogels synthesized only with acrylamide (6.5KPa) and hydrogels cross-linked with acrylamide and chitosan (21.3KPa). In addition, the results indicate that hydrogels with nanofibers are more flexible, recover up to 80% of their original height compared to hydrogels synthesized only with acrylamide (recovery of 50% of the original height) (Zhou & Wu, 2011).

in vitro methods to determine the water retention and release capacity of a hydrogel

Cortés *et al.* (2007), evaluated the release of water from acrylic based on hydrogels using a pressure plate equipment, which is used to determine soil moisture retention curves. For instance, the equipment is provided with a pressure chamber in which the wet samples are located and a porous plate, which have allowed the passage of water, the hydrogel is brought to its maximum swelling ability when is placed into the chamber, a specific pressure is applied and maintained until there is no flow of water from the chamber (Singh, Sarkar, Kumar Singh, Parsad & Singh-Parmar, 2010). The pressure values are set according to the thermodynamic soil suction potential value (average pressure exerted by a plant on the soil to absorb water)(Demitri, Scalera, Madaghiele, Sannino & Maffezzoli, 2013). It was found that the greater amount of water is released at low pressures, due to plant present greater availability to a lesser effort of the roots.

Conversely, Singh *et al.* (2010), evaluated the retention ability and pressure plate release of hydrogels synthesized from acrylamide, commercial amorphous resin (heteropolysaccharide derived from Cochlospermum species) and clay nanoparticles. Therefore, to carry out tests, mixtures of hydrogel (0.50 and 0.75% by weight) with sandy loam soil, a soil conditioner (coconut peat, vermiculite, and perlite at rate of 3: 1: 1 per volume proportions) and control sample (without hydrogel), were used. The results showed that the retained water content was higher compared to control sample with respect to the applied pressure. The water release capacity is higher for 0.75% from soil hydrogel mixtures compared to control. In this sense, a higher release capacity indicates a greater water availability of wate for the plant under conditions of water stress.

Performance evaluation of the hydrogels applied to soil

Various techniques are used to determine the performance of the hydrogel applied to soil, such as moisture retention curves, instant irrigation tests, wilt tests and plant growth tests for fast growing species (Cortés *et al.*, 2007).

More recently, Cannazza *et al.* (2014), studied the hydrogels performance with clay soils and soils with high iron content. For evaluation purpose, seedlings of chicory and tomato were used. Soil samples were prepared using hydrogel percentages between 0 and 1.5%, followed for 78 days evaluating the loss of soil moisture. In fact, hydrogels were found to improve the soil moisture retention capacity.

Liu, Liang, Zhan, Liu & Niu (2006), used soil samples from arid regions. Mixing 1g of hydrogel with 100g of soil, which was added with 250g of distilled water and the soil moisture loss was monitored for 30 days. They also carried out water infiltration tests where they used mixtures of 1g of hydrogel per 100g of dried soil, which were added with 250g of water, maintained the samples at room temperature, and the sample weight loss was assessed for nine days. Respectively, they found the evaporation percentage and soil infiltration samples based on hydrogel was lower than 41 and 55.7%, respectively compared to normal soil. Similar results were found in hydrogels synthesized from waste fiber from flax (F. Wu, Zhang, Liu & Yao, 2012). Moisture levels were

higher in sandy loam soils compared to control sample (soil without hydrogel) at temperatures of 25 and 45°C, respectively, by the addition of hydrogels obtained from clay nanoparticles. Due to an increasing water availability in the soil by hydrogels addition, the wilting point in plants was delayed up to 3.6 days (Singh *et al.*, 2010).

Given these concerns, hydrogels are an alternative to the current needs of the agricultural sector, due to majority of crops require an additional irrigation. In this sense, hydrogels have allowed an increasing in available water in the soil, which is responsible to induce a rapid plant growth, prolong the survival of plants under water stress and had achieved a controlled release of fertilizers. It was found that the trend in hydrogels research for use in agriculture is the search for methods that allows to obtain hydrogels with high swelling ability in short times, in such a way, they increase the water available in the soil. Similarly, biodegradable hydrogels and high mechanical resistance are required, presumably, hydrogels are affected by a pressure exerted by the soil layer and the plant root system pressure on the material. In fact, this provides more accurate and reliable estimates of the use of nano particles obtained from plant fibers, which have allowed to improve the swelling ability due to presence of hydrophilic groups in nanofibers, carry out the diffusion of liquid into the hydrogel matrix more efficient and fast. In addition, the addition of nanofibers in hydrogels allows an increasing in the crosslinking point density, which had achieved an improved fracture, flexural force and resistance to compression, which promotes the formation of a porous morphology, improve biodegradability, thermal stability and water retention capacity to changes of temperature in the middle.

It should be taken into account that the use of non-environmental friendly solvents used to modify natural fibers is one of the disadvantages in the hydrogels synthesis, which is why there are some literature citations on the influence of the use of microwaves and ultrasound to mitigate the impact caused by solvents. This review approached in the efficiency of hydrogels applied to the soil, which depends on soil properties such as swelling ability, mechanical resistance, soil water retention and that the fiber proportions, crosslinking point and the modifying agent, determine the hydrogel performance.

References

Abdul-Khalil, H. P. S., Bhat, A. H. & Ireana Yusra, A. F. (2012). Green composites from sustainable cellulose nanofibrils: A review. *Carbohyd Polym*, 87(2), 963–979. *http://doi.org/10.1016/j.carbpol.2011.08.078*

Agaba, H., Orikiriza, L. J. B., Obua, J., Kabasa, J. D. & Worbes, M. (2011). Hydrogel amendment to sandy soil reduces irrigation frequency and improves the biomass of Agrostis stolonifera. *Agr Sci*, 2(4), 544–550. *http://doi.org/10.4236/as.2011.24071*

Ahearne, M., Yang, Y. & Liu, K. (2008). Mechanical characterisation of hydrogels for tissue engineering applications. *Topics in Tissue Engineering*, 4, 1–16. *http://www.oulu.fi/spareparts/ebook_topics_in_t_e_vol4/abstracts/ahearne.pdf*

Aouada, F. A., de Moura, M. R., Orts, W. J. & Mattoso, L. H. C. (2011). Preparation and characterization of novel micro- and nanocomposite hydrogels containing cellulosic fibrils. *J Agr Food Chem*, 59(17), 9433–9442. *http://doi.org/10.1021/jf202347h*

Arévalo, D. (2012). Una mirada a la agricultura de Colombia desde su huella h*ídrica*. WWF (Eds.) Colombia. 48 p. *http://www.huellahidrica.org/Reports/Arevalo-2012HuellaHidricaColombia.pdf.*

Arredondo, A. (2009). Hidrogeles. Potenciales biomateriales para la liberación controlada de medicamentos. *Revista Ingeniería Biomédica*, 3(5), 83–94. *http://revistas.eia.edu.co/revistas/index.php/BME/article/view/70/70.*

Asohofrucol. (2014). Frutas & Hortalizas. *Revista de La Asociación Hortifrutícula de Colombia*, 37(Octubre), 1–40.

Bessadok, A., Marais, S., Roudesli, S., Lixon, C. & Métayer, M. (2008). Influence of chemical modifications on water-sorption and mechanical properties of agave fibres. *Composites Part A: Applied Science and Manufacturing*, 39(1), 29–45. *http://doi.org/10.1016/j.compositesa.2007.09.007*

Cannazza, G., Cataldo, A., De Benedetto, E., Demitri, C., Madaghiele, M., & Sannino, A. (2014). Experimental Assessment of the Use of a Novel Superabsorbent polymer (SAP) for the optimization of water consumption in agricultural irrigation process. *Water*, 6(7), 2056–2069. *http://doi.org/10.3390/w6072056*

Chandramohan, D. & Marimuthu. (2011). A review on natural fibers. *Int J Res Rev Appl Sci*, 8(2), 194–206. *http://www.arpapress.com/Volumes/Vol8Issue2/IJRRAS_8_2_09.pdf.*

Chang, C., Han, K. & Zhang, L. (2009). Structure and properties of cellulose/poly(N-isopropylacrylamide) hydrogels prepared by IPN strategy. *Polym Advan Technol*, 22(9).1329-1334. *http://doi.org/10.1002/pat.1616*

Chang, C. & Zhang, L. (2011). Cellulose-based hydrogels: Present status and application prospects. *Carbohyd Polym*, 84(1), 40–53. *http://doi.org/10.1016/j.carbpol.2010.12.023*

Chen, W., Yu, H., Liu, Y., Chen, P., Zhang, M. & Hai, Y. (2011). Individualization of cellulose nanofibers from wood using high-intensity ultrasonication combined with chemical pretreatments. *Carbohyd Polym*, 83(4), 1804–1811. *http://doi.org/10.1016/j.carbpol.2010.10.040*

Cortés, A. B., Xiomara, I., Ramírez, B., Francisco, L., Eslava, B. & Niño, R. (2007). Evaluación de hidrogeles para aplicaciones agroforestales. *Revista Ingeniería E Investigación*, 27(3), 35–44.

Cuéllar, A. & Muñoz, I. (2010). Fibra de guadua como refuerzo de matrices poliméricas. *Dyna*, 162, 137–142.

Delgado-Pelayo, R., Gallardo-Guerrero, L. & Hornero-Méndez, D. (2014). Chlorophyll and carotenoid pigments in the peel and flesh of commercial apple fruits varieties. *Food Res Int*, 65(B), 272–281. *http://doi.org/10.1016/j.foodres.2014.03.025*

Demitri, C., Scalera, F., Madaghiele, M., Sannino, A. & Maffezzoli, A. (2013). Potential of cellulose-based superabsorbent hydrogels as water reservoir in agriculture. *Int J Polym Sci*, 2013,1–6. *http://dx.doi.org/10.1155/2013/435073*

Dianney, D., Grimaldo, C., Edgar, J., Orjuela, A., Carmen, O. & Cardozo, A. (2010). Hacia una nueva generación de biomateriales. Primera parte. *Rev Col Or Tra*, 24(3), 168–177.

Ekebafe, L. O., Ekebafe, L. O., Ogbeifun, D. E. & Okieimen, F. E. (2011). Polymer applications in agriculture. *Biokemistri*, 23(2), 81–89.

FAO-Food and Agriculture Organization. (2013). Afrontar la escasez de agua -un marco de acción para la agricultura y la seguridad alimentaria. Informe Sobre Temas Hídricos. Roma, Italia. 97p. *http://www.fao.org/3/a-i3015s.pdf.*

Feng, H., Li, J. & Wang, L. (2010). Preparation of biodegradable flax shive cellulose-based superabsorbent polymer under microwave irradiation. *BioResources*, 5(3), 1484–1495. http://ojs.cnr.ncsu.edu/index.php/BioRes/article/view/BioRes_05_3_1484_Feng_LW_Prep_Biodegrad_Flax_Superabsorbent/653.

Gascue, B. R. De, Aguilera, R., Ramirez, M., Prin, J. L. & Torres, C. (2006). Los hidrogeles poliméricos como potenciales reservorios de agua y su aplicación en la germinación de semillas de tomate en diferentes tipos de suelos. *Revista Iberoamericana de Polímeros*, 7(3), 199–210.

Ghazali, S. K., Adrus, N., & Jamaluddin, J. (2014). Pineapple leaf fibers coated with polyacrylamide hydrogel. *Appl Mech Mater*, 695, 139–142. *http://doi.org/10.4028/www.scientific.net/AMM.695.139*

Guilherme, M. R., Aouada, F. A., Fajardo, A. R., Martins, A. F., Paulino, A. T., Davi, M. F. T., … Muniz, E. C. (2015). Superabsorbent hydrogels based on polysaccharides for application in agriculture as soil conditioner and nutrient carrier : A review. *Eur Polym J*, 72, 365–385. *http://doi.org/10.1016/j.eurpolymj.2015.04.017*

Huang, Z., Liang, X., Hu, H., Gao, L., Chen, Y. & Tong, Z. (2009). Influence of mechanical activation on the graft copolymerization of sugarcane bagasse and acrylic acid. *Polym Degrad Stabil*, 94(10), 1737–1745. *http://doi.org/10.1016/j.polymdegradstab.2009.06.023*

Hüttermann, A., Orikiriza, L. J. B. & Agaba, H. (2009). Application of superabsorbent polymers for improving the ecological chemistry of degraded or polluted lands. *Clean-Soil, Air, Water*, 37(7), 517–526. *http://doi.org/10.1002/clen.200900048*

IDEAM- Instituto de Estudios Ambientales. (2015). Informe del estado del Medio Ambiente y de los Recursos Naturales Renovables 2012 , 2013 y 2014 (Versión preliminar) Tomo III : Calidad del agua , generación de residuos y presencia de sustancias químicas en el territorio.

http://documentacion.ideam.gov.co/openbiblio/bvirtual/022651/InformeTomo3.pdf.

IDEAM- Instituto de Estudios Ambientales. (2014). Estudio Nacional del Agua 2014. *http://documentacion.ideam.gov.co/openbiblio/bvirtual/023080/ENA_2014.pdf.*

Kabiri, K., Omidian, H., Doroudiani, S. & Zohuriaan, M. (2011). Superabsorbent hydrogel composites and nanocomposites : a review. *Polym Compos*, 21, 278–289. *http://doi.org/10.1002/pc.21046*

Kalia, S., Kaith, B. S. & Kaur, I. (2014). Cellulose fibers: bio-and nano-polymer composites. *Green Chem Technol*. Springer Link (Eds.).737 p.

Krishnan K, A., Jose, C., K. R, R. & George, K. E. (2015). Sisal nanofibril reinforced polypropylene/polystyrene blends: Morphology, mechanical, dynamic mechanical and water transmission studies. *Industrial Crops and Products*, 71, 173–184. *http://doi.org/10.1016/j.indcrop.2015.03.076*

Li, Q., Ma, Z., Yue, Q., Gao, B., Li, W. & Xu, X. (2012). Synthesis, characterization and swelling behavior of superabsorbent wheat straw graft copolymers. *Bioresource Technology*, 118, 204–209. *http://doi.org/10.1016/j.biortech.2012.03.028*

Liang, X., Huang, Z., Zhang, Y., Hu, H. & Liu, Z. (2013). Synthesis and properties of novel superabsorbent hydrogels with mechanically activated sugarcane bagasse and acrylic acid. *Polymer Bulletin*, 70(6), 1781–1794. *http://doi.org/10.1007/s00289-013-0921-4*

Liu, C. F., Sun, R. C., Qin, M. H., Zhang, A. P., Ren, J. L., Xu, F. Wu, S. & Bin. (2007). Chemical modification of ultrasound-pretreated sugarcane bagasse with maleic anhydride. *Ind Crop Prod*, 26(2), 212–219. *http://doi.org/10.1016/j.indcrop.2007.03.007*

Liu, T., Qian, L., Li, B., Li, J., Zhu, K., Deng, H. & Wang, X. (2013). Homogeneous synthesis of chitin-based acrylate superabsorbents in NaOH/urea solution. *Carbohyd Polym*, 94(1), 261–271. *http://doi.org/10.1016/j.carbpol.2013.01.010*

Malherbe, S. & Cloete, T. E. (2002). Lignocellulose biodegradation: Fundamentals and applications. *Reviews in Environmental Science and Biotechnology*, 1(2), 105–114. *http://doi.org/10.1023/A:1020858910646*

Missoum, K., Belgacem, M. & Bras, J. (2013). Nanofibrillated cellulose surface modification: a review. *Materials*, 6(5), 1745–1766. *http://doi.org/10.3390/ma6051745*

Mo, C., Shu-quan, Z., Hua-min, L., Zhan-bin, H. & Shu-qin, L. (2006). Synthesis of poly (acrylic acid)/sodium humate superabsorbent composite for agricultural use. *J Appl Polym Sci*, 102, 5137–5143. *http://doi.org/10.1002/app.24661*

Mohan, Y. M., Murthy, P. S. K. & Raju, K. M. (2006). Preparation and swelling behavior of macroporous poly (acrylamide- co -sodium methacrylate) superabsorbent hydrogels. *J Appl Polym Sci*, 101, 3202–3214. *http://doi.org/10.1002/app.23277*

Nitta, S., Kaketani, S. & Iwamoto, H. (2015). Development of chitosan-nanofiber-based hydrogels exhibiting high mechanical strength and pH-responsive controlled release. *Eur Poly J*, 67, 50–56. *http://doi.org/10.1016/j.eurpolymj.2015.03.053*

Orozco-Guareno, E., Hernandez, S. L., Gomez-Salazar, S., Mendizabal, E. & Katime, I. (2011). Estudio del

hinchamiento de hidrogeles acrílicos terpolimericos en agua y en soluciones acuosas de ión plumboso. *Revista Mexicana de Ingeniería Química*, 10, 465–470.

Passaglia, E., Bertoldo, M., Coiai, S., Augier, S., Savi, S. & Ciardelli, F. (2008). Nanostructured polyolefins / clay composites : role of the molecular interaction at the interface. *Polym Advan Technol*, 19, 560–568. *http://doi.org/10.1002/pat.1107*

Pickering, K. L., Efendy, M. G. A. & Le, T. M. (2015). A review of recent developments in natural fibre composites and their mechanical performance. *Composites Part A: Appl Sci Manuf*, 83, 98–112. *http://doi.org/10.1016/j.compositesa.2015.08.038*

Pourjavadi, A. & Mahdavinia, G. R. (2006). Superabsorbency, pH-sensitivity and swelling kinetics of partially hydrolyzed chitosan-g-poly (acrylamide) hydrogels. *Turk J Chem*, 30, 595–608.

Rodrigues, F. H. A., Spagnol, C., Pereira, A. G. B., Fajardo, R., Rubira, A. F., Muniz, E. C. & Martins, A. F. (2013). Superabsorbent hydrogel composites with a focus on hydrogels containing nanofibers or nanowhiskers of cellulose and chitin. *J Appl Polym Sci*, 131(2).1–13. *http://doi.org/10.1002/app.39725*

Rodrigues, R. F., Trevenzoli, R. L., Santos, L. R. G., Leão, V. A. & Botaro, V. R. (2006). Adsorção de metais pesados em serragem de madeira tratada com ácido cítrico. *Engenharia Sanitaria E Ambiental*, 11(1), 21–26. *http://doi.org/10.1590/S1413-41522006000100004*

Rodriguez, A., Jose, V., Daniel, D., Viviane, M. & Alves Lavinia. (2014). Desarrollo de un material compuesto de fibras de henequén utilizando una matriz termofija development of composite with henequen´s fibres and termofix matrix. *Ingeniería Mecánica*, 17(3), 264–272.

Sahoo, P. K., Sahu, G. C., Rana, P. K. & Das, A. K. (2005). Preparation, characterization, and biodegradability of jute-based natural fiber composite superabsorbents. *Adv Polym Tech*, 24(3), 208–214. *http://doi.org/10.1002/adv.20042*

Sannino, A., Demitri, C. & Madaghiele, M. (2009). Biodegradable cellulose-based hydrogels: Design and applications. *Materials*, 2(2), 353–373. *http://doi.org/10.3390/ma2020353*

Shi, X., Wang, W., Zheng, Y. & Wang, A. (2014). Utilization of hollow kapok fiber for the fabrication of a pH-sensitive superabsorbent composite with improved gel strength and swelling properties. *RSC Adv*, 4(92), 50478–50485. *http://doi.org/10.1039/C4RA10866C*

Singh, A., Sarkar, D., Kumar Singh, A., Parsad, R., & Singh Parmar, B. (2010). Studies on novel nanosuperabsorbent composites: swelling behavior in different environments and effect on water absorption and retention properties of sandy loam soil and soil-less medium. *J Appl Polym Sci*, 120, 1448–1458. *http://doi.org/10.1002/app.33263*

Spagnol, C., Rodrigues, F. H. A., Neto, A. G. V. C., Pereira, A. G. B., Fajardo, A. R., Radovanovic, E., … Muniz, E. C. (2012). Nanocomposites based on poly(acrylamide-co-acrylate) and cellulose nanowhiskers. *Eur Polym J*, 48(3), 454–463. *http://doi.org/10.1016/j.eurpolymj.2011.12.005*

Spagnol, C., Rodrigues, F., Pereira, A., Fajardo, A., Rubira, A. & Muniz, E. (2012a). Superabsorbent hydrogel composite made of cellulose nanofibrils and chitosan-graft-poly(acrylic acid). *Carbohyd Polym*, 87(3), 2038–2045. *http://doi.org/10.1016/j.carbpol.2011.10.017*

Spagnol, C., Rodrigues, F., Pereira, A., Fajardo, A., Rubira, A. & Muniz, E. (2012b). Superabsorbent hydrogel nanocomposites based on starch- g -poly (sodium acrylate) matrix filled with cellulose nanowhiskers. *Cellulose*, 19, 1225–1237. *http://doi.org/10.1007/s10570-012-9711-7*

Thakur, V. K. & Thakur, M. K. (2014). Processing and characterization of natural cellulose fibers/ thermoset polymer composites. *Carbohyd Polym*, 109, 102–117. *http://doi.org/10.1016/j.carbpol.2014.03.039*

Thomas, S., Paul, S. A., Pothan, L. A. & Deepa, B. (2011). Chapter 1: Natural fibres: structure, propierties and aplications. In: Bio-and Nano-Polymer Composites (pp. 1–42). *http://doi.org/10.1007/978-3-642-17370-7*

Ullah, F., Othman, M. B. H., Javed, F., Ahmad, Z. & Akil, H. M. (2015). Classification, processing and application of hydrogels: A review. *Mater Sci Eng*, 57, 414–433. *http://doi.org/10.1016/j.msec.2015.07.053*

Vundavalli, R., Vundavalli, S., Nakka, M. & Rao, D. S. (2015). Biodegradable nano-hydrogels in agricultural farming - alternative source for water resources. *Procedia Mater Sci*, 10, 548–554. *http://doi.org/10.1016/j.mspro.2015.06.005*

Wen, Y., Zhu, X., Gauthier, D. E. & An, X. (2015). Development of poly (acrylic acid)/ nanofibrillated cellulose superabsorbent composites by ultraviolet light induced polymerization. *Cellulose*, 22(4), 2499–2506. *http://doi.org/10.1007/s10570-015-0639-6*

Wu, C.S. (2012). Preparation, characterization, and biodegradability of renewable resource-based composites from recycled polylactide bioplastic and sisal fibers. *J Appl Polym Sci*, 123(1), 347–4556. *http://doi.org/10.1002/app.34223*

Wu, F., Zhang, Y., Liu, L. & Yao, J. (2012). Synthesis and characterization of a novel cellulose-g-poly(acrylic acid-co-acrylamide) superabsorbent composite based on flax yarn waste. *Carbohyd Polym*, 87(4), 2519–2525. *http://doi.org/10.1016/j.carbpol.2011.11.028*

Zhong, K., Zheng, X. L., Mao, X. Y., Lin, Z. T. & Jiang, G. B. (2012). Sugarcane bagasse derivative-based superabsorbent containing phosphate rock with water-fertilizer integration. *Carbohyd Polym*, 90(2), 820–826. *http://doi.org/10.1016/j.carbpol.2012.06.006*