

Natural Hydrogel Synthesis, Characterization and Application: A Review

Marwa M. El Sayed¹, R. El-Araby¹, Abdelrhman A. Besheir², Abdelrhman M. Abdullah², Salma H. Ghazy², Salma S. Hamdalla^{2*}, Mayar M. Tantawy²

¹Chemical Engineering and Pilot Plant Department, National Research Center, Cairo, Egypt El-Bohouth Street, Dokki; P.O. Box 12622 Phone: +201115079146, Fax: +20-2-3370931,

²Department of Chemical Engineering, Higher Technological Institute, Tenth of Ramadan City, Egypt *email

ABSTRACT

Hydrogels are three-dimensional structures made up of organic materials that are weakly cross-linked and have a high to extremely high aqueous swelling ability. Hydrogels are a class of polymeric materials with a hydrophilic structure that allows them to store huge amounts of water in three-dimensional networks. The widespread use of these goods in a variety of industrial and environmental applications is seen as critical. Natural hydrogels were gradually phased out in favor of synthetic hydrogels, which have a better water absorption capacity, a longer service life, and a wider range of chemical raw material. The previous work on the field of hydrogel is growing, particularly in scientific fields of study. However, a number of articles and technical studies dealing with hydrogel products from an engineering standpoint were investigated in order to gain a broad overview of the technological features of this rapidly expanding multidisciplinary field of study. The major goal of this paper is to examine the literature on natural-base hydrogels, including their physical and chemical properties, as well as their applications.

KEY WORDS: Hydrogel, Natural Polymer, Synthesis, Characterization, Applications.

Date of Submission: 15-06-2021

Date of Acceptance: 30-06-2021

I. INTRODUCTION

Hydrogels have drawn special attention in the past 30 years due to their exceptional use in biomaterials applications. The hydrogel is a water-swelled, crosslinked polymeric network that results from a simple reaction of one or more monomers or via hydrogen bonds and strong van der Waals interactions between chains (Marta, 2019). Another definition of hydrogel is that, it is a polymeric material which exhibits the ability to swell and retain a significant amount of water without dissolving. The three-dimensional network structures of hydrogel can be formed by the introduction of intermolecular cross-links linear polymer chains. The cross-links can be formed by covalent bonds, or electrostatic, hydrophobic, or dipole-dipole interactions, Rituraj Singh & Vikas Mahto (2017).

Hydrogels have been reviewed in many research papers, and each article has shown a specific look. For example, the preparation and properties of the hydrogel formulation were reviewed, as well as the discussion of hydrogel network sources such as synthetic, semi-synthetic and biopolymer hydrogels (El-Sayed, 2017). In this article the hydrogel chemistry and various synthetic

preparation procedures are comprehensively reviewed.

Another review article discussed in detail the methods of preparing hydrogel networks, highlighting hydrogels used in field soil conditioners that were prepared from synthetic polymers.

Moreover, natural polymers such as polysaccharides and proteins have been used as raw materials for preparing hydrogels. This was mentioned in an exclusive article published in 1994 presenting the patent literature with a careful review of water-absorbing polymers and their use in industrial production.

Stanford Research Institute has released a user profile for industrial applications where SRI Hydrogels have been prepared using the family of acrylic monomers.

Two notable books on synthetic hydrogels were published between 1990 and 1998 in which the main phenomena related to synthetic hydrogels were clearly reflected (Chen, 2021). One of the well-known, available and effective methods for preparing hydrogels, especially when using natural polymers, is the free radical grafting polymerization of the monomer in a single polymer chain. The

kinetics of radical graft polymerization of monomer on polysaccharide chain has been studied (OU & BO, 2017).

Hydrogels can be made from virtually any water-soluble polymer, including a wide range of chemical compositions and bulk physical properties. Furthermore, hydrogels can be formulated into a variety of physical forms including sheets, microparticles, nanoparticles, coatings and films. Hydrogels have been widely used as drug carriers due to their ease of manufacture and self-application in clinical and basic applications, (Tanan, 2018). Hydrogel can be produced either from natural or synthetic polymers from this material point of view.

In terms of material cost, natural polymer hydrogel has been distinguished because it is less expensive in addition to biocompatibility and biodegradability, while composite polymer hydrogel is more difficult than natural in both the source, techniques and application.

However, the natural polymer hydrogel is more notable due to its lower cost, good biocompatibility and biodegradability. Synthesized

polymer hydrogel is more challenging than natural in terms of source, techniques, and application.

Hydrogels are commonly used in industries such as medicine, horticulture, and agriculture. There are different ways to classify hydrogels based on their materials, technologies, and applications. The standard technique used to induce crosslinking is a chemical or physical technique and polymerization (Sarah, 2021). In the current review hydrogel prepared using a platform of natural polymer has been discussed in details including preparation techniques, characterization and the main applications.

II. CHITOSAN

Chitosan (CH) is a linear polysaccharide, has β -(1-4)-linked d-glucosamine and N acetyl-d-glucosamine units. CH is a **natural polymer** (Fig.1) obtained mostly from the shells of sea animals as chitin. Chitin is sourced from the exoskeletons of crustaceans such as shrimps, lobsters, and crabs (OU & BO, 2017).

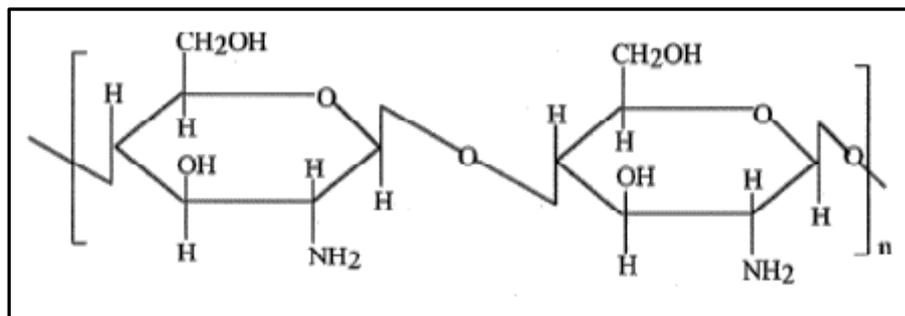


Figure (1): Chitosan polymer

Chitosan is one of the most often used materials in the production of hydrogels, and it has been evaluated for use in wound dressings. It has good biocompatibility, minimal toxicity, and immune-stimulating properties. Due to these properties, Chitosan has strong biocompatibility and has a beneficial effect on wound healing. It can also speed up the healing of various tissues and make wound contraction easier. (Hamedi, 2018)

Chitosan's vast range of uses is attributable not only to its exceptional biocompatibility, biodegradability, and cost-effectiveness, but also to its unique chemical structure, which has a high percentage of primary amino groups (-NH₂) allowing facile binding to biomolecules including DNA and proteins. **Table (1)** will show the principal applications of chitosan-based hydrogel. (Rinaudo, 2006)

Table (1) Principal applications of chitosan-based hydrogel

Agriculture	<ul style="list-style-type: none"> • Defensive mechanism in plants • Stimulation of plant growth • Seed coating, Frost protection. • Time release of fertilizers and nutrients into the soil
-------------	--

Water & wastetreatment	<ul style="list-style-type: none"> • Flocculant to clarify water (drinking water, pools) • Removal of metal ions • Ecological polymer (eliminate synthetic polymers) • Reduce odors
Food & beverages	<ul style="list-style-type: none"> • Not digestible by human (dietary fiber) • Bind lipids (reduce cholesterol) • Preservative • Thickener and stabilizer for sauces • Protective, fungi static, antibacterial coating for fruit
Cosmetics & toiletries	<ul style="list-style-type: none"> • Maintain skin moisture • Treat acne • Improve suppleness of hair • Reduce static electricity in hair • Tone skin • Oral care (toothpaste, chewing gum)
Biopharmaceutics	<ul style="list-style-type: none"> • Immunologic, antitumoral • Hemostatic and anticoagulant • Healing, bacteriostatic

2.1 Chitosan-based Hydrogel Preparation

Graft copolymerization is an effective method for structural modification of hydrogels with desired functional groups. It is worth noting that it is possible to obtain the molecular design that matches the appropriate application by grafting the functional monomers onto the polymer backbone, as the absorption capacity of the hydrogels can be significantly changed and modified either by adding functional groups or increasing their density. The most prominent examples of these groups are, Amino, sulfur, carboxyl and alkyl (Meng, & Cheng, 2019).

There are three types of conventional monomers used to graft hydrogels: non-ionic, cationic, and anionic (Suh, 2016).

Key parameters such as the type and concentration of the initiator, inoculation time and temperature, as well as the type and concentration of monomers also influence (Jingli, 2020). Many common monomers have been grafted on chitosan in the hydrogel synthesis as acrylic acid, acrylamide, itaconic acid, (Galal Ibrahim, 2019). However, most high molecular weight chitosan is insoluble in water caused by strong intramolecular hydrogen bonding, which hinders the applications. To overcome the limitation, functional addition of hydrophilic groups on the amine and hydroxyl group is a convenient

approach to tune the solubility (Meng, et al., 2019) synthesized a new bioactive photothermal hydrogel based on N,O-carboxymethyl chitosan incorporated fayalite (Fe_2SiO_4), which can release bioactive ions with mild heating function in the wound area to promote angiogenesis and chronic wound healing (Sampath et al. 2017).

By grafting the polymerization of acrylamide (AAM) onto a chitosan backbone (CTS), hydrogel polymers were prepared in the presence of methylenebis acrylamide (MBA) as a cross-linking agent and ammonium sulfate (APS) as an initiator. The grafting process increased the swelling of the grafted product, which showed swelling of 260 g/g polymer, and the highest equilibrium swelling was attained by utilizing a 1 % cross-linker ratio relative to acrylamide. (Galal Ibrahim, 2019)

Hydrogel polymers were prepared by using two natural polymers Carboxymethyl cellulose (CMC) and Carboxymethyl chitosan (CMCts) grafted by Sodium styrene sulfonate (SSS) to give super absorbent hydrogels (SAHs) by using gamma-irradiation Figure (2). Swelling ratio will be (2500 g/g) at 0.32 mol/l for SSS. This hydrogel can be used in pharmaceuticals, agriculture, and the food industry and even in hygienic products. (Hong et al, 2018).

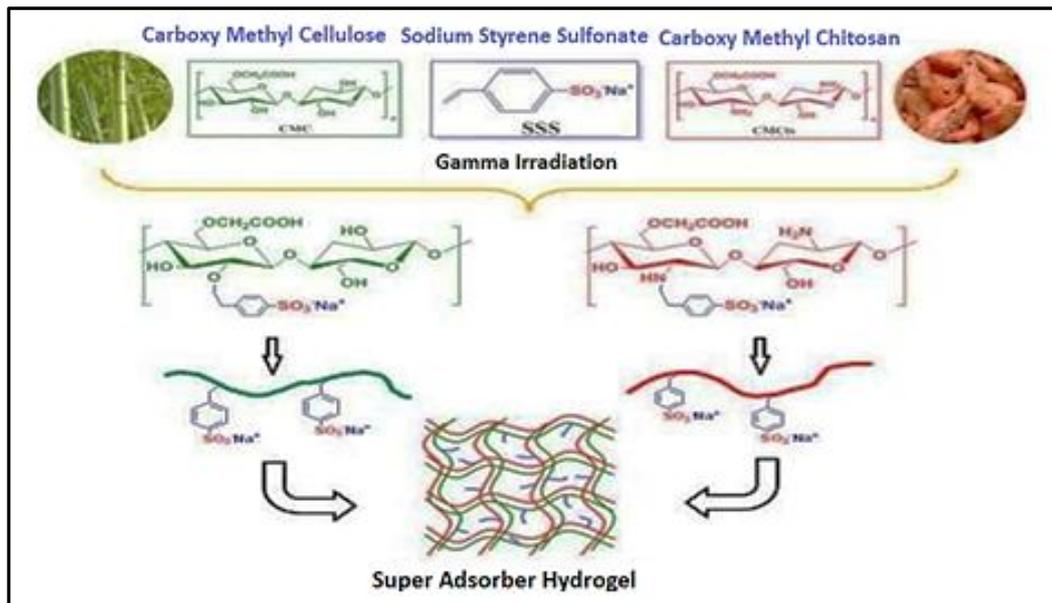


Figure (2): Proposed scheme for the forming Super Adsorber hydrogel

Hydrogel composed of chitosan-grafted acrylamide-co-acrylic acid monomers has been synthesized using ceric ammonium nitrate as an initiator and methylene bis acrylamide as crosslinker. Hydrogel samples have been prepared, that 4g of chitosan has been dissolved in 140 ml. Then, 1 g of ceric ammonium nitrate (CAN), 16 g of acrylamide (AAm), and 4 ml acrylic acid (AA) mixtures have been added. Four different weights of MBA (0.1, 0.3, 0.5 & 0.7 g) have been added. The highest swelling water ratio values were 54, 51.86, and 38.8 g/g. Use the prepared hydrogel in the adsorption of the reactive dyes from real wastewater sample collected from a textile factory.

(Sampath, 2017 & El-Sayed, 2017)

Superabsorbent hydrogels have been prepared using chitosan (CH) grafted poly (acrylic acid) (PAA) in presence of potassium persulfate (KPS) as initiator and N, N'-methylene bis acrylamide (MBA) as a cross-linker as shown in Fig. (6). Because of the greater purity and crystallinity, hydrogels filled with RHA previously calcinated at 900 °C (RHA900) demonstrated superior water absorption (225 g water/g absorbent) than those filled with husk previously calcinated at 400 °C (198 g water/g absorbent). (Rodrigues, et al., 2012)

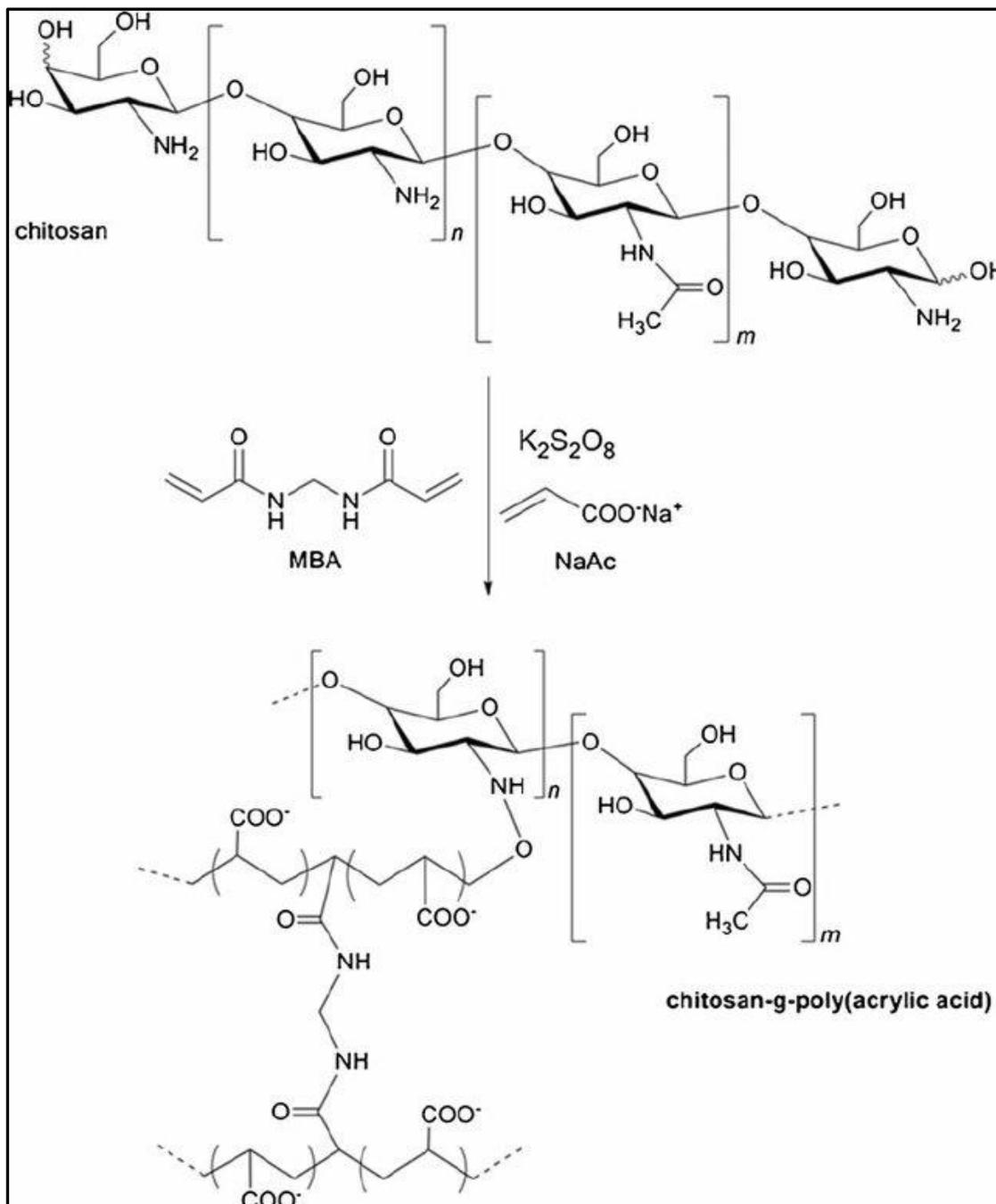


Figure (3): Schematic chemical graft reaction of PAA onto CTS backbone and crosslinking reaction of MBA)

Acrylamide and cationic natural biopolymer chitosan were used to prepare Semi-interpenetrating hydrogels in presence of MBA and water-soluble redox initiating system (APS/MBA).

The swelling ratio increases by increases of chitosan concentration that in different swelling media such as water, nonionic, cationic and anionic surfactant solutions, the max swelling reached to 17g/g, in different swelling media due to the increases of a number of hydrophilic groups(-OH)

present in the chitosan. (Varaprasad, et al., 2010)

A series of excellent hydrogels were prepared from poly (vinyl alcohol) (PVA) and carboxymethylated chitosan (CM-chitosan) with electron beam irradiation (EB) at room temperature. These blends between natural and synthetic polymers are investigated extensively because they can be used as biomedical and biodegradable materials. PVA/CM-chitosan blend hydrogels had upgraded tensile strength and elongation. The addition of CM-

chitosan/PVA hydrogels is predicted to modify and improve their characteristics. This hydrogel has acceptable antibacterial activity against E.coli, making it suitable for application in biomedicine and pharmacy. At 10% PVA and 3% CMCs and at 20 dos (KGy), Swelling ratio will be 30 (g solvent /g dry gel). (Zhao, et al., 2003)

UV irradiation of solutions in moderate aqueous acid medium of poly- (ethylene glycol)

The above-mentioned studies and investigations are briefly shown in Table (2), by presenting different types of polymers and monomers, if used, to produce the hydrogel with

macromer (PEGM) with chitosan in the presence of glutaraldehyde as a crosslinking agent produced interpenetrating polymer network (IPN) hydrogels. Using a 450 W UV lamp, UV irradiation was used to polymerize and crosslink PEGM inside the crosslinked chitosan network. This hydrogel will use to transdermal drug delivery matrix or wound dressing materials. (Lee, Kim, & Lee, 2000).

starch. Also types of initiators and crosslinkers, optimum conditions, characterization techniques, swelling% and applications of each hydrogel were mentioned.

Polymer	Monomer	in	CL	Swelling (g/g)	Technique	Application	Reference
CTS	AAm	APS	MBA	325	Conventional	wastewater treatment.	(Galal Ibrahim, 2019)
CMC CMCs	SSS			2500	γ -irradiation	wastewater treatment.	(Hong, 2018)
Chitosan	AAm acrylic acid (AA)	CAN	MBA	54	Conventional	wastewater treatment	(El-Sayed, 2017)
CTS	AA	KPS	MBA	225	Conventional	medical and sanitary materials,	Rodrigues, 2012)
chitosan	AAm		MBA	17	Conventional	Drug Delivery	Varaprasad, 2010)
CNCs			Glutaraldehyde	220%	Ultrasonic	tissue engineering, pharmaceuticals, and drug delivery	(Sampath, 2017)

Table (2). Chitosan -based hydrogels

III. STARCH

Starch (St) is the most abundant storage polysaccharide in plants, and it appears in granules known as starch grains in the chloroplast of green leaves and the amyloplast of seeds, pulses, and tubers. (Ismail, Irani, & Ahmad, 2013). Starch is a tasteless and odorless white powder in its raw form. It is made up of a huge number of glucose units that

are bonded together by glycoside bonds. In general, starch appears in two forms shown in Figure (4): linear and helical amylose α -(1-4)-linked D-glucose monomers (20-25% w/w) and branched amylopectin (a highly branched polymer composed of both α -(1-4)- and α -(1-6)-linked D-glucose monomers) (75-80%). (Chen Y., 2019).

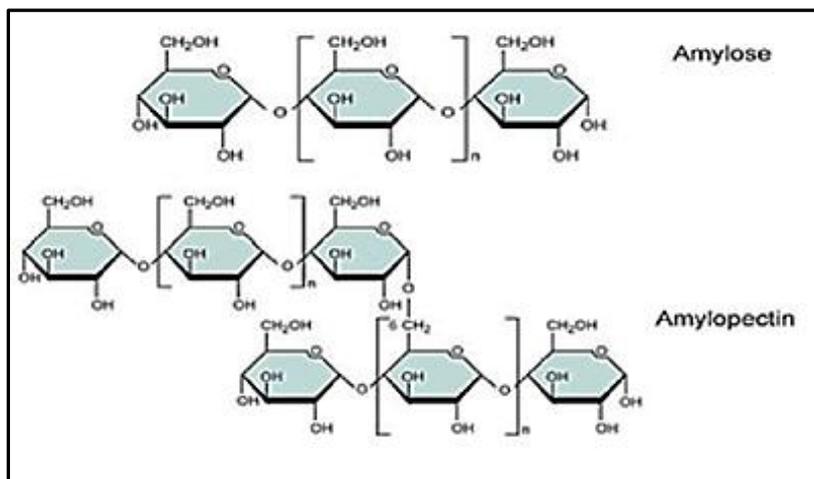


Figure (4): Structure of amylopectin and amylose in starch

Apart from amylose, a semi-crystalline biopolymer which is soluble in hot water, amylopectin is a highly crystalline polymer that is insoluble in hot water. Although the concentration of these two components varies depending on the source of starch (e.g., corn, potato, tapioca, wheat), the microstructure of starch is the same (Chen Y., 2019).

As starch is one of the important polysaccharides, kind of native and renewable polymer. It is useful in industrial applications (e.g., adhesives, papers, mulch films, packaging, clothing and

biodegradable plastics) because of its low cost, renewable nature, and biocompatibility. (Meng, et al., 2020). Native starch properties may not be suitable for all applications. However, there are several methods for modifying the properties of starch to suit certain purposes. Physical, chemical, and enzymatic modifications are among these methods. (Qamruzzaman, 2021)

One of the most remarkable and common applications of starch is starch-based hydrogels. Starches with a number of hydroxyl groups can be used to prepare hydrogels easily. Hydrogels have been prepared using chemical processes such as etherified starches and grafted starches. Some hydroxyl groups of starch are replaced by ether groups in etherified starches, such as sodium carboxymethylstarch (CMS-Na). In grafted starches, different vinyl monomers, such as acrylamide and acrylic acid, can be grafted onto starch. (Ismail, Irani, & Ahmad, 2013)

It appears that the advantages of using starch, particularly its biodegradability, outweigh the disadvantages. This is because, in recent years, more focus has been placed on reducing environmental issues caused by the usage of

synthetic polymers. (Ismail, Irani, & Ahmad, 2013) Starch-based hydrogels has a wide variety of applications, such as: dye absorption, biomedical applications, tissue engineering, agricultural uses, drug delivery systems and wastewater treatment.

As mentioned before starch-based hydrogels can be synthesized chemically by different methods and techniques to offer the proper characteristics that support those variety of applications.

A double-network hydrophobic-hydrogel was successfully synthesized from starch and polyacrylic acid and using epichlorohydrin (ECH) and N, N-methylenebisacrylamide (MBA) act as the crosslinkers. The amphoteric characteristics of the hydrogel with both positive and negative charge were used to exclude cationic and anionic dyes from waste aqueous solution. Positive charge is formed in the hydrogel by the interaction of triethylamine with the open up epoxy ring of ECH, whereas negative charge is formed by the carboxylate ion of polyacrylic acid. The presence of quaternized alkyl chains and the formation of double cross-linking result in hydrophobicity with substantially reduced swelling capacity. The hydrogel proved effective as an adsorbent for both cationic dye (methylene blue) and anionic dye (Congo red), with adsorption maxima of 134 mg/g and 65.45 mg/g, respectively. This study showed that the synthesized hydrogel has significant promise as a toxic dye adsorbent for industrial wastewater effluent treatment. (Sarmah & Karak, 2020).

(P S Puspita 2019) used cassava starch (CSt) to natural polymer-based nanohydrogel synthesis. This study modified starch using acid hydrolysis method for 2 hours and 24 hours, which is shown in the SEM images in Figure (5). After that, the ethanol precipitation method is used to create nano-particle starch. Gamma irradiation was

used to initiate the formation of nano-hydrogels. The results showed that the size of starch nanoparticles was between 14.97 - 492.7 nm, and hydrolysis time affected the crystallinity of starch. Gamma irradiation reduces the swelling of nano-hydrogels

(from 365.47% to 256.81%), increases the gel fraction, and enhances the mechanical strength of the texture. (Puspita, Winarti, Maddu, & Kurniati, 2019).

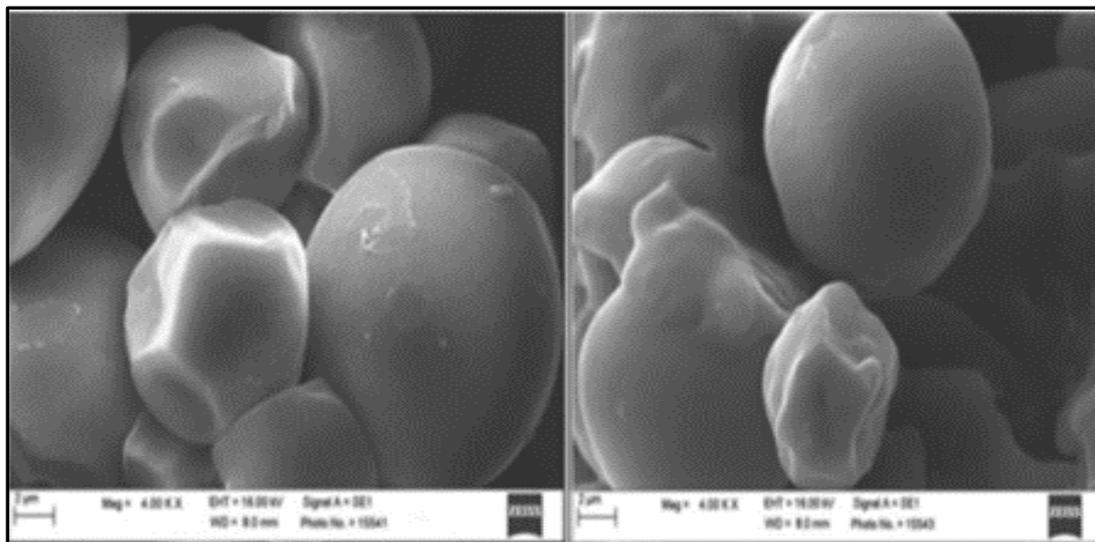


Figure (5): SEM morphology of hydrolyzed starch (R) 2 hours and (L) 24 hours

A new starch-based nano-hydrogel complex reinforced with chemically modified natural char particles (NCNPs) has been synthesized and has proven cost-effectiveness.

The study started with the preparation and characterization of virgin natural coal (NC) and its various modified structures through mechanical ball milling (BMNC) method and chemical oxidation. The results demonstrated that the performance of the composite was controlled by the filler properties (i.e. morphology shown in the SEM images in Figure (6), size, surface chemistry and functions)

and NCNPs with the smallest particle sizes (14.8–3.0 nm) and higher oxygen functions were chosen as the best candidate. stuffing. The coexistence of physical and covalent bonding in the NCNPs/Hydrogel nanocomposite can be proposed as the reason for the two-fold (389.9 g/g) water absorption compared to the elegant hydrogel (202.1 g/g). The high water-retention capacity of NCNPs/Hydrogel nanocomposite, in addition to its natural origin, widened its potential applications as an eco-friendly and economical agricultural hydrogel. (Motamedi, 2019).

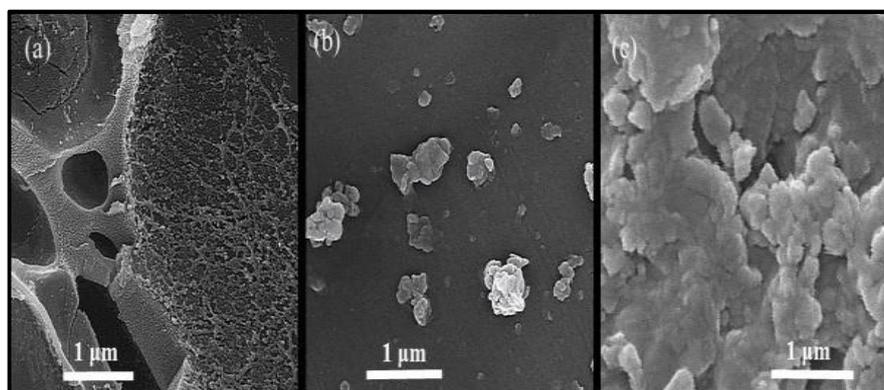


Figure (6): SEM images of hydrogel (nano)composites containing of (a) NCNPs, (b) BMNC, and (c) NC fillers

Another novel eco-friendly and low-cost semi- interpenetrating polymer network (semi-IPN)

hydrogel of cassava starch-g-polyacrylic acid/natural rubber/polyvinyl alcohol blends (CSt-g-

PAA/NR/PVA) was developed. The contents of several components such as CSt, AA, cross-linking agent (MBA), and initiator (CAN) have had a significant impact on the hydrogels' water absorbency and water-retention behavior. The water swellings of the optimal end product in distilled water and 0.9 wt% NaCl solution were 794 and 244 %, respectively, under optimum conditions. The semi-IPN hydrogel demonstrated a good

biodegradation with a rate of 0.626 wt%/day. Morphology of the hydrogel, shown in Figure (7), was observed by (SEM). The obtained hydrogel could have potential applications in agricultural areas because of their good water absorption, high retention capacities, high reswelling capability, and cost-effective and ecofriendly preparation. (Tanan, 2018).

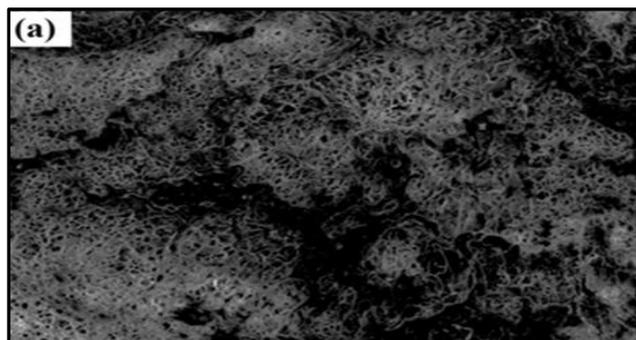


Figure (7): SEM micrograph of the hydrogel sample at 200x magnifications

Fekete et al. studied the effect of the addition of starch on the properties of carboxymethylcellulose-based super absorbent hydrogels prepared by gamma irradiation. The starch granules and fragments were dispersed in the CMC matrix, and the swelling of CMC/starch gels was highly sensitive to water ionic strength due to the CMC component, but less than pure CMC gels. Hydrogels containing 30% starch demonstrated the

best properties, with a water absorption 350 g/g achieved with a ~55 % gel fraction synthesized from 15% w/w solutions at 20 kGy. SEM photographs of freeze-dried CMC/starch hydrogels with different starch content is shown in Figure (8). Depending on the application, CMC/starch hydrogels may be a more cost-effective and better option than pure cellulose derivative-based gels. (Fekete, 2017).

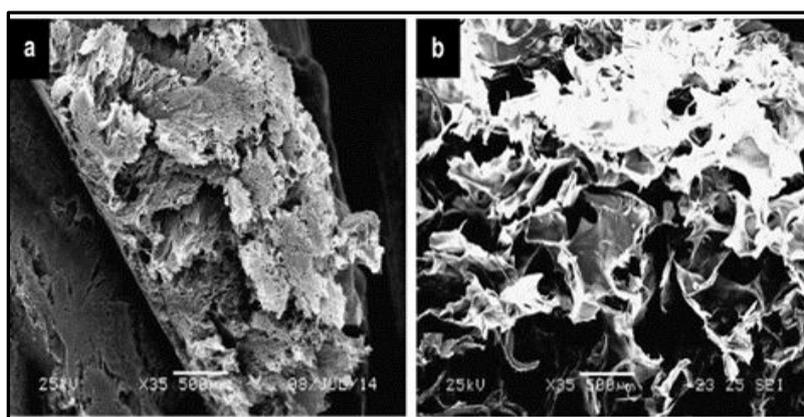


Figure (8): SEM photographs of freeze-dried CMC/starch hydrogels with a starch content of 0% a, 30% b

The fabrication of starch-based hydrogels to combine the controlled release and water absorption (WA) of soils has been investigated where the function of the hydrogel in this case is to carry carbendazim. This type of hydrogel was loaded with starch in two steps, and in one slow release system was combined with WA. (Cheng et

al. 2015). First gelatinized starch was mixed with an amount of carbendazim which was dissolved in 1.5 mL of AA, and the resulting solution was introduced into a reaction flask containing 9 mL of ddH₂O and 1.5 mL of MMA to form the bead, the product was labeled as mixture 1. Second step was preparing CLH by mixing the remaining

gelatinized starch with AA, Am, KPS and MBA then blend it with mixture 1. The CLHs were characterized by SEM image of St-g-(MMA-co-AA) beads is shown in Figure (9). The WA capacities could reach 800 g of ddH₂O and 160 g of tap water per gram of CLH. (Bai, 2015)

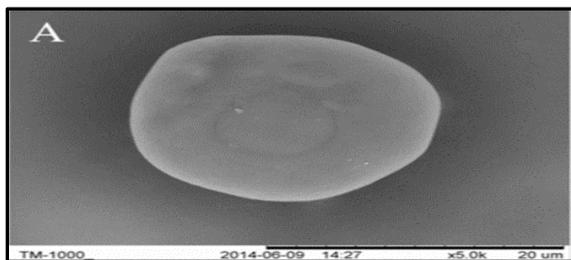


Figure (9): SEM images of starch-g-(MMA-co-AA) beads

Polymer network (IPN) hydrogel based on crosslinked natural rubber (NR) latex and crosslink

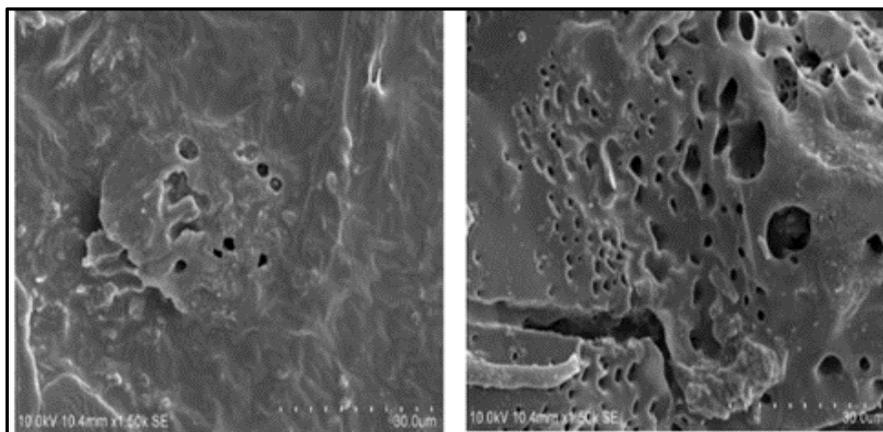


Figure (10): SEM micrographs of IPN NR/St with rubber/starch ratio of (R) 50/50 and (L) 70/30 after buried under soil for 1 month.

Cassava starch has been used to examine the effect of natural rubber (NR) on the properties of a biopolymer hydrogel produced from polyacrylamide (PAM) and starch (St) using maleic anhydride MA as a cross-linking reagent with microwave assistance. The key parameters that impacted the characteristics of the hydrogel samples were studied, including the polymer blend ratio, the NR concentration, and the (MA) content. The swelling of the polymer hydrogel film samples decreased as the St and NR contents increased. However, when the quantity of PAM in the sample increased, the swelling ratio of the polymer hydrogel increased. Depending on the parameter conditions, the swelling ratio of the polymer hydrogels ranged from 10 to 17 times. This novel polymer hydrogel has potential applications in the fields of medicine and agriculture (Riyajan, 2013).

cassava starch (CSt) by a solution blending technique. Crosslinked NR latex was firstly prepared in emulsion state at 70°C by using potassium persulfate as initiator and (MBA) as crosslinker. Secondly, the crosslinked NR latex was mixed with gelatinized cassava starch and maleic acid (MA) as crosslinker for starch. Water absorption, soluble fraction, biodegradation, and tensile properties all decreased as NR concentration increased, but gel fraction in water and elongation at break increased. This was due to the fact that the rubber molecules prevented the hydrogel from dissolving in water and being degraded by microorganisms. The SEM images, shown in Figure (10), of IPN NR/St after buried under soil for 1 month showed many granular holes of St dispersed in rubber matrix. This confirmed that NR can be used to reduce the degradation of St. (Vudjung et al. 2014).

The adsorption of metal ions Cu²⁺ and Ni²⁺ from contaminated simulated water using new starch/acrylamide-based hydrogels in the presence of lignin or peat to create an interpenetrating polymer network (IPN) has been studied. Hydrogels were prepared by adding the synthetic monomer AA to the natural polymers in the presence of ammonium peroxydisulfate as an imitator and MBA as a crosslinking agent. The chemical structure of the materials was studied using (FTIR) and their morphology, shown in Figure (11), was observed by (SEM). Most of the hydrogels showed maximum water absorption values at about 100 h, when it reached the equilibrium. And they have a high potential to obtain metal ion-collector membranes. (Peñaranda & Sabino, 2010)

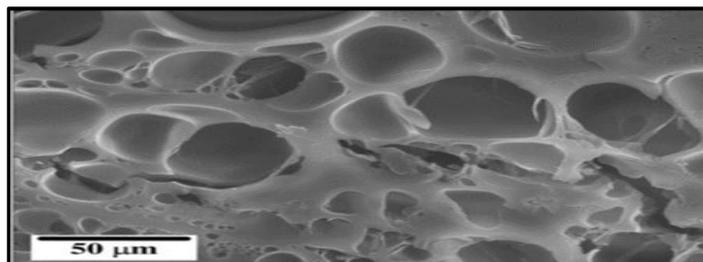


Figure (11): SEM micrograph of internal morphology of hydrogel formulation.

The above-mentioned studies and investigations are briefly shown in Table (3), By presenting different types of polymers and monomers, if used, to produce the hydrogel with

starch. Also types of initiators and crosslinkers, optimum conditions, characterization techniques, swelling% and applications of each hydrogel were mentioned.

Table (3). Starch-based hydrogels

Polymer	Monomer	Initiator	CL	Technique	Swelling	Applications	Ref.
St.	AA	APS	ECH MBA	Conventionall	Low WA	Dye absorption	Sarmah, 2020
CassavaSt		Γ- radiation	-	Gammaradiation	~375%	-	Puspita, 2019
(NC)	AAm AA	APS	MBA	Ultrasonic	390 g/g	Agriculture	Motamedi, 2019
(CSt)	(AA)	(APS)	(MBA)	Conventionall	575	Agriculture	Tanan, 2018
CMC Potato st	-	-	MBA	Gamma radiation	350	drug delivery system	Fekete, 2017
St.	AA MMA AAm	KPS	MBA	Conventionall	800	Agriculture	Bai, 2015
CSt	-	KPS	MBA	Conventionall	102.75	Agriculture	Vudjung, 2014
HANR (CSt) (PAM)	-	-	MA	Microwave radiation.	23	Medicine Agriculture	Riyajan, 2013
Lignin CSt	AAm	APS	MBA	Conventionall	1250%	metal ion- collector membranes.	Penaranda, 2010

IV. ALGINATE

Alginate is a water-soluble polysaccharide isolated from the cell walls of Laminaria, Macrocystis, and Ascophyllum species of brown algae. Alginate's inherent hydrophilicity makes it a great gel-forming chemical that can store a lot of water. Alginate is a natural polysaccharide with high biocompatibility and gel-forming characteristics (Sahoo & Biswal, 2021).

ability, non-toxicity, biodegradability, and processability Alginate and its hydrogel form are employed in a variety of biomedical applications,

including medication delivery, wound healing, and tissue engineering, due to their superior characteristics. (Alihosseini, 2016)

Brown algae and some bacteria create alginate, a linear polymer that serves as an ECM component. The polysaccharide is made up of repeating units of 4-D-mannuronic acid (M) and α-L-guluronic acid (G) Fig. (15), which form a hydrogel when the G residues are ionic cross-linked in the presence of a divalent cation. Figure (12). (Patino, 2013)

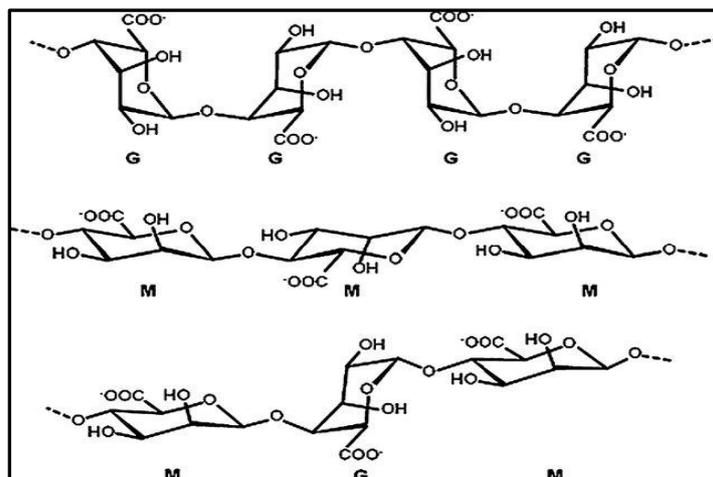


Figure (12): Chemical structure of G-block-block, and alternating block in alginate

The crosslinking reagent for alginate is calcium chloride (CaCl_2) solution, which provides an external gelation approach for making alginate beads Figure (13). When alginate solution is dropped into CaCl_2 , a 3-D network of highly

hydrated gel forms quickly. Sodium chloride (NaCl) is frequently added to the CaCl_2 solution to provide anti-gelling cations and improve the homogeneity and porosity of the resultant alginate gel. (Patino, 2013, Farhad ,2020)

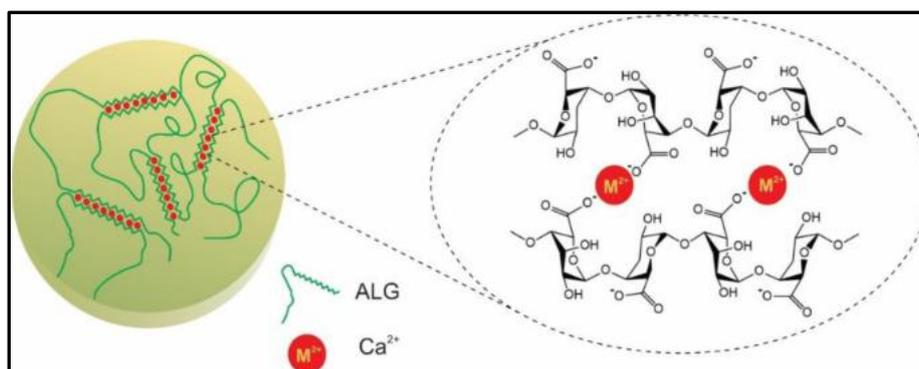


Figure (13): Alginate hydrogels prepared by ionic cross linking

The chemical and physical properties of the Ca^{2+} -crosslinked alginate hydrogels resulted in improved adhesion to wounds, allowing for a wide range of applications in hemostasis and wound healing, such as the generation of hemostatic needles by simply coating the syringe needles surface with the hydrogel, which can stop bleeding. Through an in-situ solid-to-gel phase transition. Alginate solution (1.5 wt. %) was prepared using conventional techniques by dissolving 75 mg of sodium alginate in 4.925 g of deionized water, and then 100 mg of the initiator CaCl_2 (1 wt.%)) was added in the above Solution and stirring at 10-20 °C. FTIR , SEM and AFM were used to characterize the produced hydrogel samples. Alg-Ca solid film coating will not be peeled off the needle before reaching the puncture site, according to swelling test results; however, the film can easily separate

from the needles and attach to the puncture sites following in-situ swelling. (Jingli, 2020)

Combining chitosan with alginate, which are both significant macromolecules for tissue engineering, improves their mechanical properties, allowing them to be used in cell development. The chitosan stock solution was made using conventional technique in 100 mL of 0.5 M acetic acid. 2 g chitosan powder was first suspended in dS-tilled water at 120°C and acetic acid was added, after which 2 g sodium alginate was dissolved in 100 ml at room temperature until a homogeneous solution was achieved. Swelling test results indicate that 3500-6000 % (Kemal, 2013)

Natural polymer hydrogels have a variety of qualities that replicate the original extracellular matrix and provide microenvironments that retain cellular function and foster tissue growth in soft

tissue engineering. A tri-component hydrogel including collagen, alginate, and fibrin (CAF) was created and tested for use as a functional extra at three different collagen concentrations. For the synthesis of the hydrogel chitosan was prepared using conventional technique, as a calculated amount of Collagen (0.5%, 1% and 2.5% w/v), Alginate (5%) and Fibrin (10% w/v) that incubated at 37 °C. Samples were then tilted every 5 min and classified as either a solution incubated at 37 °C. Swelling test results indicate that between 3000 and 4000% (Montalbano, 2018)

The treatment of industrial effluents is highly desirable due to the presence of numerous toxics, nonbiodegradable and water-soluble dyes which adversely affect living organisms and the environment. The treatment of these contaminants by using hydrogel sorbents may be a fascinating approach due to facile operation, high efficacy, simple synthesis, rapid recovery and subsequent reuse of hydrogels. The Sodium alginate grafted poly (N-vinyl formamide-co-acrylic acid)-bentonite clay hybrid hydrogel in the application of removal of methylene green from wastewater. As the mixture of sodium alginate (SA), poly(N-vinyl formamide-co-acrylic acid)-bentonite clay, the initiator ammonium per sulphate (APS) and the crosslinker N,N-methylene bisacrylamide (MBA) carried out by free radical polymerization, in steps first stirring of sodium alginate, and bentonite clay solution at 60° C, heating of mixture of SA-bentonite clay, and APS at 60 ° C; finally drying the hybrid material to dissolve the unreacted monomer at 40°C. The produced hydrogel has swelling test results indicate that 8049% at pH 11. (Subhan, 2021)

A Semi-IPN superabsorbent hydrogels

based on sodium alginate-g-poly (sodium acrylate) and polyvinylpyrrolidone is synthesized and can be used in many applications such as Agriculture, Waste water treatment, and Drug delivery system (Wang & Wang, 2010). A pH-sensitive semi-interpenetrating polymer network (semi-IPN) superabsorbent hydrogel composed of sodium alginate-g- poly (sodium acrylate) (NaAlg-g-PNaA) network and linear polyvinylpyrrolidone (PVP) was prepared by free-radical solution polymerization in the presence of initiator APS and MBA. The total neutralization degree of 65%, and then 18 mg crosslinker MBA was dissolved in the partially neutralized acrylic acid (NaA . FTIR and SEM were used to characterize the produced hydrogel samples. (Wang & Wang, 2010)

V. CELLULOSE

Cellulose is a natural polymer which has been discovered for first time in 1838 by Anselme Payen, the French chemist, through extraction it from plant matter, also cellulose structure determined. Cellulose is the material that appears abundantly on earth, and it forms an important part of cell walls in higher plant. Cellulose can be extracted from different sources, such as; sugarcane, sorghum bagasse, corn stalks, and straws of rye, wheat, oats, and rice, also it's the main component in; cotton (95%), flax (80%), jute (70%), and wood (50%). (Rojas, 2016) Cellulose considered as; organic linear polysaccharide, that formed from D-glucose units, that have a formula $(C_6H_{10}O_5)_n$. Figure (17) shows the structure of cellulose, and in case of absence of side chains in molecule of cellulose, a rigid structure formed due to that side chains closed to each other (Chen Y. , 2020).

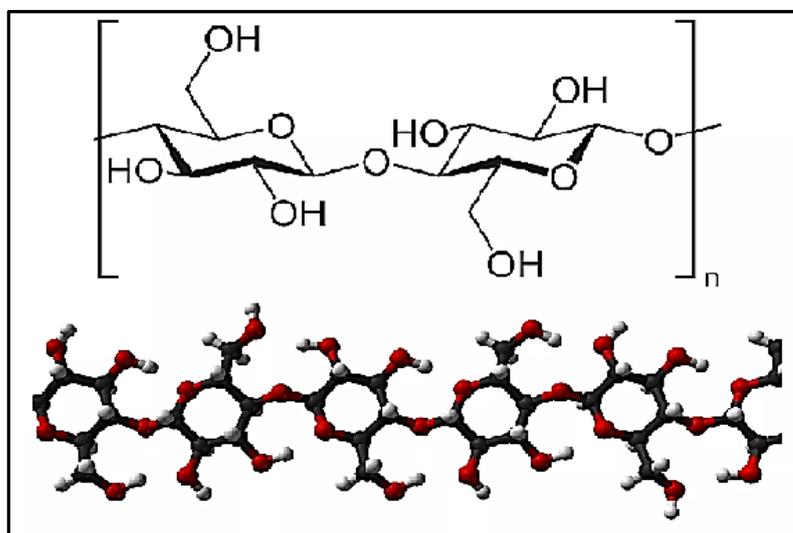


Figure (14): Structure of cellulose.

Cellulose is a solid, biodegradable polymer, with no toxicity, it has swelling for different polar liquids, including water, as it distinguished that it's hygroscopic substrate, that can absorb from 8% to 14% of water, at 20°C, and relative humidity 60%. Determination of mechanical properties of cellulose depend on; its crystallinity, polymerization degree, orientation degree of microfibrils, to fiber axis, also, its

arrangement of microfibrils in fiber, and finally microfibrils

size, and shape (Suhass, 2016). Cellulose tensile increases with increasing crystallinity, polymerization degree, and orientation degree. Values of tensile properties; strength, and elastic modulus of some cellulose sources are shown in Table (4) (Jean-Luc,2010).

Table (4). Values of tensile properties of different cellulose sources

Cellulose source	Tensile strength (GPa)	Elastic Modulus (GPa)
Flax	0.34-1.03	27-100
Jute	0.39-0.77	26-65
Ramie	0.40-0.94	60-128
Cotton	0.28-0.6	5-13
Wood	1	10-40

Physical properties of cellulose, that will be showed, is its thermal, electrical, and optical properties. Cellulose can be considered as a semicrystalline polymer, distinguished as it's non melting, and non-thermoplastic polymer, with thermal degradation up to 180°C. Above this temperature cellulose amorphous regions will be in glassy state, (Rojas, 2016, Jean-Luc Wertz, 2010).

Swelling of cellulose can be done by two methods, dependence on degree of penetration of reagents for cellulose structure. Some reagents such

as; water, and organic liquids, can penetrate amorphous region of cellulose structure which known as; intercrystalline swelling. Some other reagents such as; alkali metal hydroxides, Ammonia, hydrazine, amines, inorganic acids, and salts, can penetrate cellulose structure completely, which known as; Intracrystalline Swelling (Jean-Luc Wertz, 2010). Cellulose used for preparation of many types of hydrogels, for many applications. Which summarized in Table (5).

Table (5). Some hydrogel prepared from cellulose, and their processes conditions, and applications

Polymer	Monomer	Applications	References
Microcrystalline cellulose	Acrylamide	Removal of Cr(VI)	(Yin,2020)
Carboxymethyl cellulose (CMC)	Aniline	electrically Conductive hydrogel	(Junrong, 2017)
Cellulose	2- acrylamido-2- methylpropanesulfonic acid Acrylic acid (AA)	Superabsorbent Hydrogel	(Wei-Min, 2015)
CMC	graphene oxide (GO)	PH-sensitive hydrogel	(Hongjie, 2019)
CMC & CH	Citric acid (CA)	Sustainable environmentally hydrogel	(Kindness, 2020)
CMC	Polyvinyl acetate (PV A)	Selective Adsorption of Copper(II) Ions	(Chanathi,2018)

VI. OTHER NATURAL POLYMERS

Many different types of natural polymers have been used in the hydrogel production in the following section some of them will be illustrated.

6.1. Guar Gums

Guar gum is macromolecule which was formed from carbohydrates and it is one of the galactomannans which was obtained from *Cyamopsis tetragonoloba*. Guar gum's structure is complex and it has high molecular weight that forms from 2-3 KDa that the units of mannose can be arranged by using linear fashion which is β -D

(1-4) the linkage of glycoside and units of galactose were attached by using α -D (1-6) the linkage of side unit and with ratio 2:1, Guar gum was attached easy with water because of presence the groups of OH, that forms bonds of hydrogen that showed increasing in the share rate but decreasing in the viscosity, Guar gum is neutral polymer, hydrophilic and non-ionic polymer, Guar gum and its derivatives has many applications so it is used in food industry, textile printing, explosives, the products of the smoking, papers and pharmaceuticals, the Figure (15) will show the structure of guar gum.

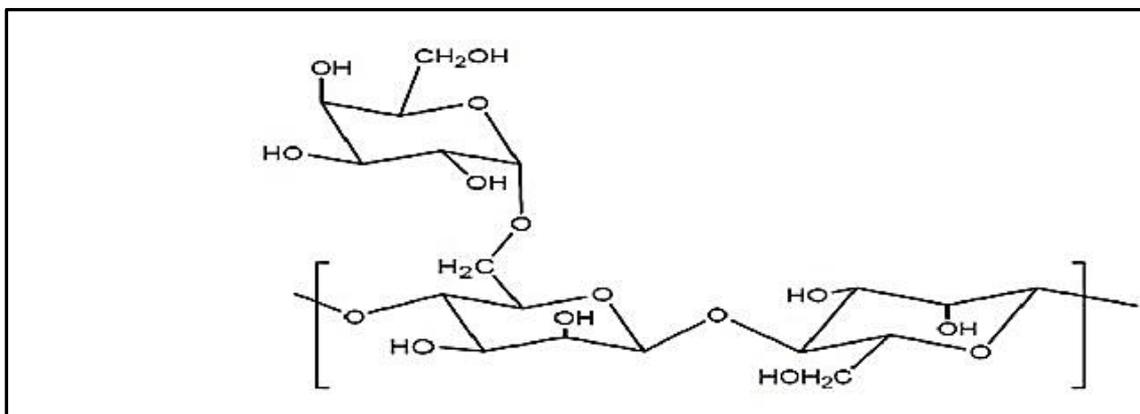


Figure (15): Structure of guar gum

Guar gum is considered as polysaccharides, this type of polymer is grafting before using it to manufacture the hydrogel, the grafted polymer is used with cross-linker which is acrylic acid and other cross-linker acid which is ethylene glycol di methacrylate and using initiator which is benzoyl peroxide.

The grafting reaction occur at nitrogen atmosphere in closed container with inlet and outlet nitrogen gas with amount of guar gum is one gram, The solution is heated from 5 to 6 minutes this heating occur to remove oxygen which is dissolved and using stirrer for this reaction, The stirring initiator benzoyl peroxide and cross-linker ethylene glycol di methacrylate dissolved in acrylic acid, this reaction formed mixture, this mixture stirred for ten minutes in water path for two days at temperature 60 C° to facilitate hydrogel forming (Thombare, 2017).

There are many studied tests to determine the capacity of swelling with distilled water with ration 1 gm of guar gum to 80 ml of distilled water, the density of the cross-linker is considered major factor because it controls on the hydrogel swelling, If it is small change in the density of the cross-linker it change the rate of the swelling, when the

swelling decrease for 0.5 mM in its concentration that make the cross-linking is insufficient that will make the partial dissolution of this hydrogel in the solution so it make the hydrogel becomes poor in its mechanical lacks and more poor for retaining the water, when the concentration of ethylene glycol di methacrylate become 0.5mM the swelling index is also decreased due to increasing of the density of the cross-linking hydrogel which makes decreasing in the spaces between the network (Thombare, 2017).

There are thermal studies occur to for guar gum and the cross-linker which is used, this study determines the nitrogen atmosphere which is inert has range from 25 C° to 620 C° with rate of heating 5 C° per minute. The solid state analysis occur by using NMR, and the record of the spectra on JEOL is 400 MHz, this analysis occur at temperature 25 C° and 9.38 T at MAS frequency 10 KHz (Thombare, 2017).

The study of biodegradation for the manufactured hydrogel occur by using method of soil burial, the hydrogel put in nylon bags to be buried in the soil at deep from 6 cm to 8 cm and maintained the moisture in the soil at 1/3 of its capacity to retention the water after certain time get

out the bags and washing it to remove the soil then there is calculation the degradation percentage it is calculated for the weight of the hydrogel which remaining in the soil in that time The advantage of this type that is may be used instead of the polymers which is synthetic because it is non-toxicity, Guar gum based hydrogel is used in many industries such as medical and agriculture (Thombare, 2017).

6.2. Lignin

This polymer is considered one of three components which form the walls of the cells of natural lignocellulose and this polymer is considered the most second polymer in world, 30%

of the carbon which is organic in the natural is from lignin, this polymer is produced as byproduct in many industrials such as paper industry and pulp industry, Lignin is very important polymer so is used to produce material which has high value instead of burning due to its nature properties as toxicity is low, eco friendless and biocompatibility, Lignin is composed of three monomers of phenyl propane, *p*-coumaryl alcohol, simply alcohol and coniferyl alcohol, After the pulping process the lignin which is produced from it, is called liginosulfonate, kraft lignin and organosolv lignin, the Figure (16) will show the structure of lignin (Meng, 2019).

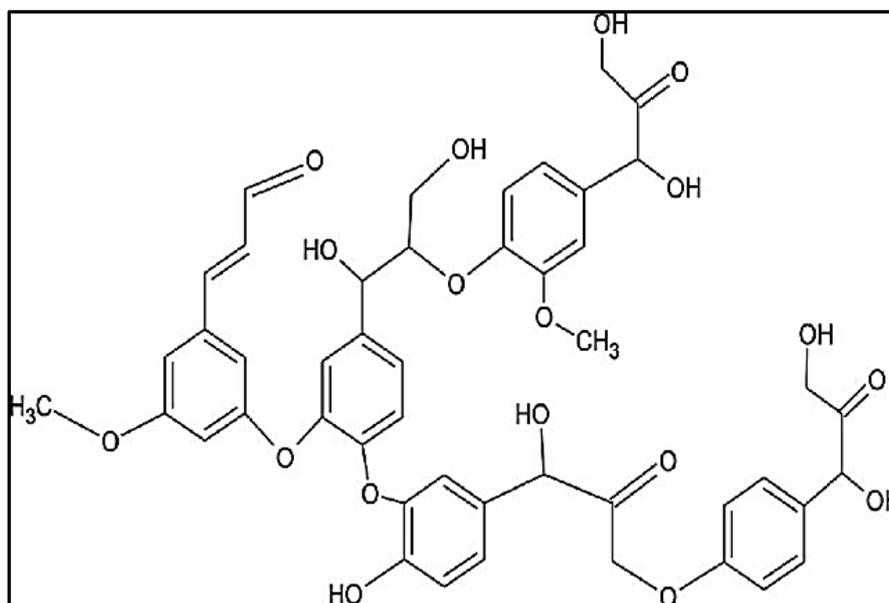


Figure (16): The lignin structure

Using lignin polymer to be in the network of the polymer by interpenetrating to be used for hydrogel manufacturing with new functions but the origin properties of the lignin polymer is kept, this process is used free radical polymerization to manufacture the hydrogel, in this process the

phenolic hydroxyls of lignin polymer react with monomers in presence of initiator makes radicals and form grafted polymer that make the interpenetrating network, the free radical reaction will show in Figure (17).

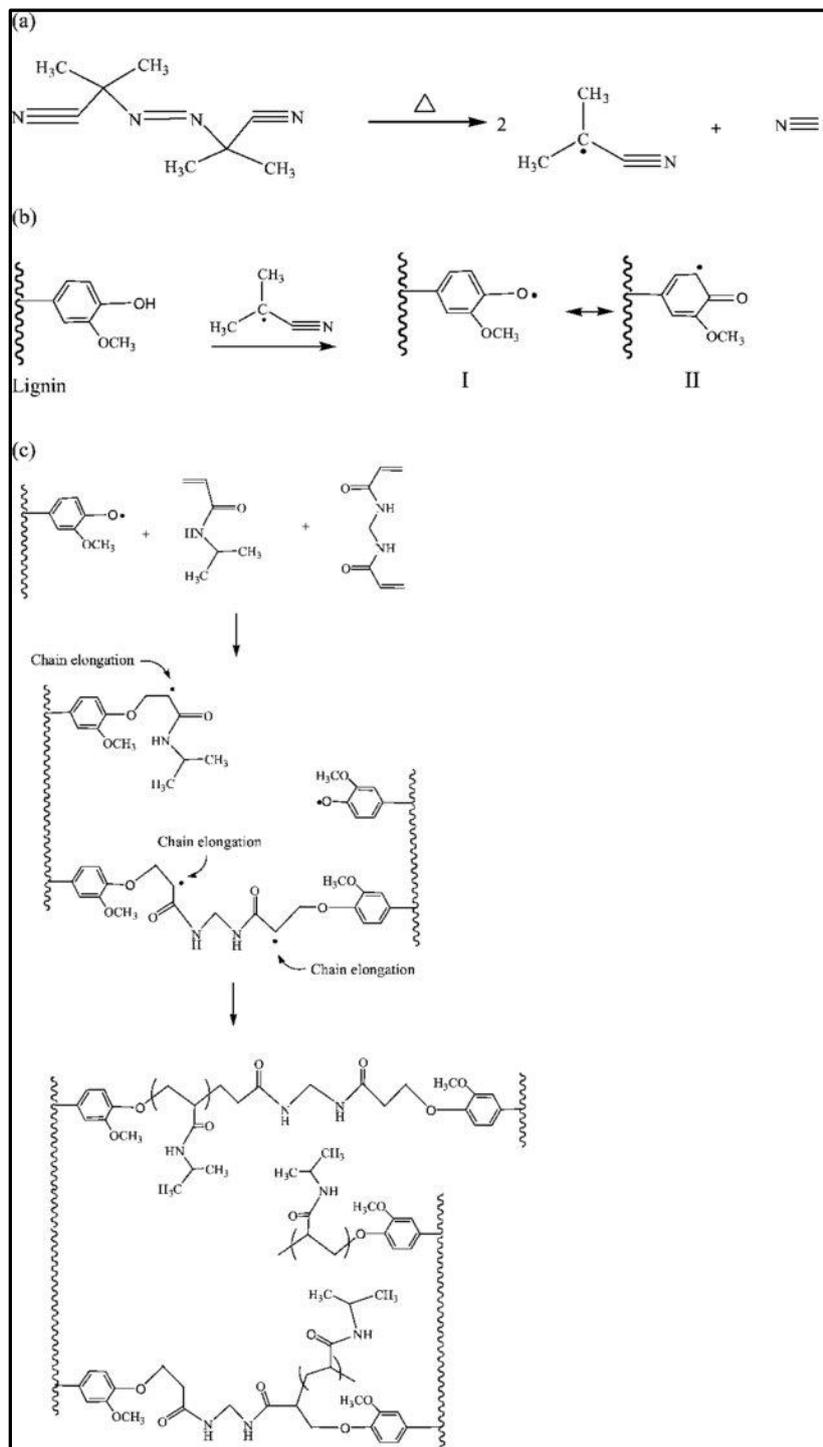


Figure (17): The free radical polymerization for lignin

There is another simple method to prepare lignin-based hydrogel by making copolymerization of cross-linkers with lignin in this method the reaction occurs between lignin and its derivatives with cross-linkers as paraformaldehyde and formaldehyde with catalysis to make the structure of the network, in this method the hydrogel was prepared by using two steps the first one the

dissolved lignin, polyethylene glycol and aqueous ethanol this mixture is heated to be evaporated by to form the film by using oven at 80 C^o for 24 hr so the polymerization reaction occur, the reaction occur in solid phase and it is free from solvents. (Meng, 2019)

The lignin polymer has many properties such as rheological this property was known at

temperature 25 °C due to its structure it is rigid network, hydrogels have dynamic storage modulus that the loss modulus, the dynamic storage modulus is increasing with the hydrogel which content lignin this result from the lignin backbone which is rigid that make the cross-linking degree increase and the makes increasing in the rigid of the network structure (Meng, 2019).

Another property is biodegradability, this property makes the hydrogel based of lignin is suitable for using it in agriculture due to its ability to improve the quality of soil by saving the roots of the plant from the microbes, this property is based on the phenolics content in the hydrogel and the density of the cross-linked.

Lignin based hydrogel is biodegradability, compatibility and biodegradation it makes its uses in wide fields so it uses in production of bio materials as agriculture, water treatment and water retention (Meng, 2019).

6.3. Arginine (based Poly ester amide)

Arginine is very important for the mammals which is young due to its rule in the nitration suppliers that is help in development for the tissues such as the regeneration of the bone, the regeneration of the bone occur when charge of arginine is positive could make interaction between calcium (Ca⁺) and Phosphate (Po₄)⁻³ this reaction produce hydroxyapatite (HAP) which help by forming crystals, this polymer may also help in the improving the density of the minerals in the bones (Zhoua, 2019).

Many of the compounds which contain hydrogen is used for preparing the tissues such as polyamines, nitric oxide, creatine and agmatine all of this compounds is produced from metabolism of the arginine polymer, Arginine based polyester amide (Arg-PEA) is mixture of blocks of amides, blocks of ester and finally the residues of arginine, polyester has many properties such as biocompatibility, the mechanical strength, biodegradability and its thermal stability is excellent for polyamide, arginine polymer in the compound (Arg-PEA) has the same functions but by using the hydrolysis reaction it might realize the release the arginine, the properties of the positive charge the solubility of (Arg-PEA) the biological properties and physical properties could be increased for the materials of the bones (Zhoua, et al., 2019).

The manufacturing of the hydrogel is based on arginine poly ester amide and HA-MA with difference in their ratios, this compounds is dissolved in distilled water which is di-ionized then dissolved the photo initiator which is hydroxyl methyl- propiophenone in the amount of DMSO so this temperature stirred and irradiated to UV lamp with has long wavelength for certain time this process occur at temperature of room, this hydrogel which is obtained was put in the distilled water for 48 hr at the room temperature to remove any chemicals and to reach for the equilibrium of the swelling then it dried for 48 hr in the temperature of the room, Table (6) will show the composition of hydrogel (Zhoua, 2019).

Table (6). Compositions of the hydrogel

Sample	Arginine-PEA	HA-MA	Photo initiator	Di-ionized water
HA-MA	0	0.1	1	1
5% PEA/HA-MA	0.05	0.1	1	1
10% PEA/HA-MA	0.1	0.1	1	1
15% PEA/HA-MA	0.15	0.1	1	1

The swelling test occur for this hydrogel for three days at the temperature of room, but before this test the hydrogel was weighted then this hydrogel was immersed in PBS at 5 ml for determined time.

The degradation test also occurs in the solution of PBS, in this test the hydrogel was washed and immersed in PBS at 10 ml then it put in oscillator

with temperature 37C° and constant rate of shaking is 50 rpm, this hydrogel is washed to remove the chemicals finally it was weighted and the degradation is recorded. (Zhoua, 2019)

6.4. Collagen

The collagen polymer is hydrolyzed and

produced component with high solubility that is used in many industries such as the industry of food and the industry of cosmetic in the production of skin care, when collagen polymer is hydrolyzed with the products of nutrients it may produce bio-fertilizer that could be used in many fields, This polymer is also used to increase the biodegradability for the plastic materials when it added to synthetic polymers, it is used as cross-linker to increase the mechanical properties. The collagen polymer could be treated such as sponges,

films and skin grafts (Stefan, et al., 2020).

The hydrogel based collagen might be manufactured by using hydrolysis process of the waste of the belt because there are large amount of treated leathers produced from the waste of the belts, The properties of the hydrogel based collagen and its stability increases by using cross-linkers such as polyacrylamide or by using some components such as polyepoxy, formaldehyde, acyl azides and glutaraldehyde, Figure (18) will show the collagen structure (P. K.& Dandge, 2018)

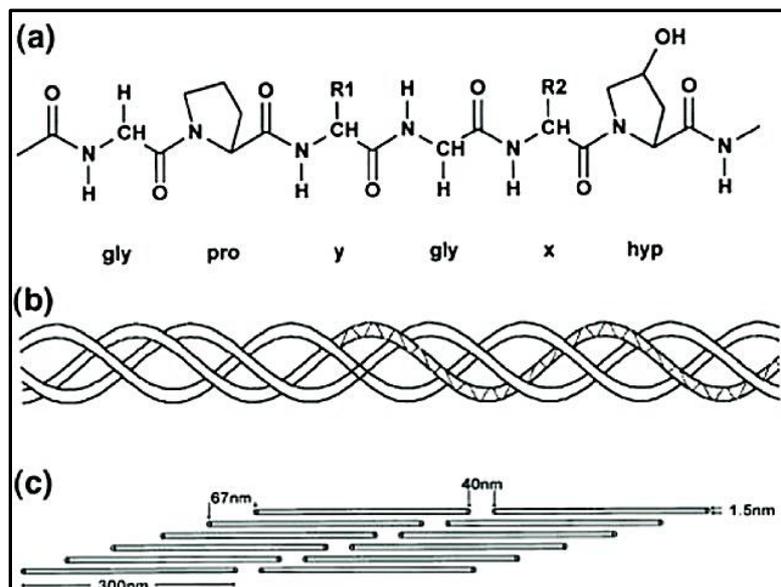


Figure (18): Collagen structure

In the preparation of hydrogel-based collagen there are raw materials used such as wastes of limed hide which is obtained from fleshing and trimming bovines hide. The preparation of collagen occur through the hydrolysis reaction for the hide of gelatin in the presence of potassium phosphate and using the protein which is hydrolysate with the polymers as acrylamide starch, cellulose and polyvinyl alcohol to manufacture the fertilizers (Stefan, et al., 2020).

The manufacturing of hydrogel-based collagen occurs in steps, the first step is obtaining the matrix of the collagen by using hydrolysis reaction to the hide of the gelatin at determined time range from 90 min to 210 min at range of temperature from 86 C° to 90 C° with H₂SO₄ at range 2.7% to 3.6%

The second step is adding the collagen which is hydrolysate with the nutrients of PK by using treatment method with solution of K₂HPO₄ its concentration is from 10% to 20%. The third step in parallel, preparing other polymeric solution of the acrylamide or using starch by mixing it continuously then this mixture is added MBA. The collagen is

hydrolyzed by using copolymerization acrylamide, finally obtaining the hydrogel-based collagen. The hydrolysate of the collagen has many uses such as proteins to the young animals, The collagen is used in the fertilizers and has another industry use for medical but the collagen used for two industries is not same there is difference between them in the step of drying, in the medical industry the drying occur by using atomization, this could not be applied in the collagen for fertilizers industry because it degrades easy in the air and will be rotted (Stefan, 2020).

VII. CONCLUSION

The present work aims to briefly introduce some hydrogels from the class of natural polymeric materials. This class of hydrogels has the advantage of having the ability to retain huge amounts of water due to its special structure and subsequent swelling properties. Chitosan, Starch, Alginate and Cellulose are the most popular types of natural hydrogel, in addition to some other types such as Guar Gums, Lignin, Arginine and Collagen. The former types have the advantage of their special structure and

subsequent swelling properties which has led to increased demand for them for use in a variety of applications, and due to the possibility of modifying the polymeric structure to obtain the desired functions, the fields of applications are expanding rapidly. Synthesis design and manufacture of new natural hydrogels are related to the nature of specific functions that meet specific needs, and this is done by manipulating the chemical composition, cross-linking method or morphological features, which leads to the production of a new and intelligent hydrogel. It can also be designed in such a way that it responds to a specific stimulus including pH, temperature, light, etc. at a predetermined level and thus the stimuli are responsive. Among its amazing properties, biocompatibility and biodegradability make it a strong candidate for use in various biological and environmental applications. Many aspects related to the mechanical properties and preparation of these type of aqueous natural polymers remain to be improved in order to enhance these products in various applications.

REFERENCES

- [1]. Alihosseini, F. (2016). Plant-based compounds for antimicrobial textiles. *Antimicrobial Textiles*.
- [2]. Bai, C., Zhang, S., Huang, L., Wang, H., & Ye, Q. (2015). Starch-based hydrogel loading with carbendazim for controlled-release and water absorption. *Carbohydrate Polymers*, 376–383. doi:http://dx.doi.org/10.1016/j.carbpol.2015.03.004
- [3]. Chanathi Baiya, L. N. (2018). The Synthesis of Carboxymethyl Cellulose-Based Hydrogel from Sugarcane Bagasse Using Microwave-Assisted Irradiation for Selective Adsorption of Copper (II) Ions. *Environmental Progress & Sustainable Energy*.
- [4]. Chen, L., Zhu, Y., Cui, Y., Dai, R., Shan, Z., Chen, H., (2021). Fabrication of Starch-Based High Performance Adsorptive Hydrogels Using a Novel Effective Pretreatment and Adsorption for Cationic Methylene Blue Dye: Behavior and Mechanism. *Chemical Engineering Journal*, 405 (1), 126953.
- [5]. Chen, Y. (2019). *Hydrogels Based on Natural Polymers*. China: Elsevier. Chen, Y. (2020). *Hydrogels Based on Natural Polymers*. Cambridge : Elsevier .
- [6]. Devi, N., Sarmah, M., Khatun, B., & Maji, T. (2017). Encapsulation of active ingredients in polysaccharide–protein complex coacervates. *Advances in Colloid and Interface Science*, 239, 136-145.
- [7]. El-Sayed, M., Bazed, G., & Abdel-Fatah, M. (2017). Development of a Novel Hydrogel Adsorbent for Removal of Reactive Dyes from Textile Effluents. *Research Journal of Pharmaceutical, Biological and Chemical Sciences*, 945-955.
- [8]. Farhad Abasalizadeh , Sevil Vaghefi Moghaddam , Effat Alizadeh , Elahe Akbari , Elmira Kashani , Seyyed Mohammad Bagher Fazljou , Mohammadali Torbati , Abolfazl Akbarzadeh,(2020). Alginate-based hydrogels as drug delivery vehicles in cancer treatment and their applications in wound dressing and 3D bioprinting. *National Library of Medicine*.
- [9]. Fekete, T., Borsa, J., Takács, E., & Wojnarovits, L. (2017). Synthesis of carboxymethylcellulose/starch superabsorbent hydrogels by gamma-irradiation. *Chemistry Central Journal*. doi:10.1186/s13065-017-0273-5
- [10]. Galal Ibrahim, A. (2019). Synthesis of Poly(Acrylamide-Graft-Chitosan) Hydrogel: Optimization of The Grafting Parameters and Swelling Studies. *American Journal of Polymer Science and Technology*, 5(2), 55.
- [11]. Hamed, H., Moradi, S., Hudson, S., & Tonelli, A. (2018). Chitosan based hydrogels and their applications for drug delivery in wound dressings: A review. *Carbohydrate Polymers*, 199, 445-460.
- [12]. Hong, T., Okabe, H., Hidaka, Y., & Hara, K. (2018). Radiation synthesis and characterization of super- absorbing hydrogel from natural polymers and vinyl monomer. *Environmental Pollution*, 242, 1458-1466.
- [13]. Hongjie Daia, Y. Z. (2019). Synthesis and response of pineapple peel carboxymethyl cellulose-g-poly (acrylic acid-co-acrylamide)/graphene oxide hydrogels. doi:https://doi.org/10.1016/j.carbpol.2019.03.090
- [14]. Ismail, H., Irani, M., & Ahmad, Z. (2013). Starch-Based Hydrogels: Present Status and Applications. *International Journal of Polymeric Materials and Polymeric Biomaterials*, 411-420.
- [15]. Jean-Luc Wertz, O. B. (2010). *Cellulose Science and Technology* . Lausanne: E P F L P r e s s .
- [16]. Jingli, R., Xingjie Yin, Y. C., Yu Chen, H. S., Ke Wang, L. Z., & Jintao. (2020). Alginate hydrogel-coated syringe needles for rapid haemostasis of vessel and viscera puncture. *Biomaterials*. doi:10.1016/j.biomaterials.
- [17]. Junrong Li, L. F. (2017). Preparation of conductive composite hydrogels from

- carboxymethyl cellulose and polyaniline with a nontoxic crosslinking agent. *RSC Advances*, 7(86), 54823–54828. doi:10.1039/c7ra10788a
- [18]. Kemal, B., b, A. Z., Aroguzc, Z. A., & Bahattin M, B. (2013). Chitosan/alginate crosslinked hydrogels: Preparation, characterization and application for cell growth purposes. *International Journal of Biological Macromolecules*. doi:10.1016/j.ijbiomac.
- [19]. Kindness A. Uyangaa, O. P. (2020). Citric acid crosslinked natural bi-polymer-based composite hydrogels: Effect of polymer ratio and beta-cyclodextrin on hydrogel microstructure. *Reactive and Functional Polymers*.
- [20]. Lee, S., Kim, S., & Lee, Y. (2000). Interpenetrating polymer network hydrogels based on poly(ethylene glycol) macromer and chitosan. *Carbohydrate Polymers*, 41(2), 197-205.
- [21]. Marta Calvo Catoira, Luca Fusaro, Dalila Di Francesco, Martina Ramella & Francesca Boccafoschi. (2019). Overview of natural hydrogels for regenerative medicine applications. *Biomaterials Synthesis and Characterization*.
- [22]. Meng, R., Wu, Z., Xie, H.-Q., Xu, G.-X., Cheng, J.-S., & Zhang, B. (2020). Preparation, characterization, and encapsulation capability of the hydrogel cross-linked by esterified tapioca starch. *International Journal of Biological Macromolecules*.
- [23]. Meng, Y., Lu, J., Cheng, Y., Li, Q., & Wang, H. (2019). Lignin-based hydrogels: A review of preparation, properties, and application. *International Journal of Biological Macromolecules*, 57.
- [24]. Montalbano, G., Toumpaniari, S., Popov, A., Duan, P., Chen, J., Dalgarno, Ferreira, A. (2018). Synthesis of bioinspired collagen/alginate/fibrin based hydrogels for soft tissue engineering. *Materials Science and Engineering: C*. doi:10.1016/j.msec.2018.04.101
- [25]. Motamedi, E., Motesharezedeh, B., Shirinfekr, A., & Samar, S. (2019). Synthesis and swelling behavior of environmentally friendly starch-based superabsorbent hydrogels were reinforced with natural char nano/micro particles. *Journal of Environmental Chemical Engineering*, 103583.
- [26]. OU A., & BO, I. (2017). Chitosan Hydrogels and their Glutaraldehyde-Crosslinked Counterparts as Potential Drug Release and Tissue Engineering Systems - Synthesis, Characterization, Swelling Kinetics and Mechanism. *Journal of Physical Chemistry & Biophysics*, 07(03).
- [27]. P. K., & Dandge, P. (2018). Collagen and collagenolytic proteases: A review. *Research gate*.
- [28]. Patino, C. (2013). Alginate Hydrogel as a Three-dimensional Extracellular Matrix for In Vitro Models of Development. *Biological Systems Engineering at DigitalCommons University of Nebraska*.
- [29]. Peñaranda, A.; Jesús, E.; Sabino, M.A. Effect of the presence of lignin or peat in IPN hydrogels on the sorption of heavy metals. *Polym. Bull.* 2010, 65, 495–508.
- [30]. Peñaranda, J. A., & Sabino, M. A. (2010). Effect of the presence of lignin or peat in IPN hydrogels on the sorption of heavy metals. *Polymer Bulletin*, 495-508. doi:http://dx.doi.org/10.1007/s00289-010-0264-3.
- [31]. Puspita, I., Winarti, C., Maddu, A., & Kurniati, M. (2019). Synthesis of cassava starch based nano- hydrogels using gamma irradiation. *IOP Conf. Series: Earth and Environmental Science*, 299. doi:10.1088/1755-1315/299/1/012009
- [32]. Qamruzzaman, M., Ahmed, F., Mondal, M., (2021). An Overview on Starch-Based Sustainable Hydrogels: Potential Applications and Aspects. *Journal of Polymers and the Environment*, https://doi.org/10.1007/s10924-021-02180-9
- [33]. Rinaudo, M. (2006). Chitin and chitosan: Properties and applications. *Progress in Polymer Science*, 31(7), 603-632.
- [34]. Rituraj Singh & Vikas Mahto.(2017). Synthesis, characterization and evaluation of polyacrylamide graft starch/clay nanocomposite hydrogel system for enhanced oil recovery. *Original Paper*.
- [35]. Riyajan, S.-A. (2013). Effect of natural rubber on polymer hydrogel produced from polyacrylamide and starch using the microwave method. *ELASTOMERS AND PLASTICS*, 23-28.
- [36]. Rodrigues, F., Fajardo, A., Pereira, A., Ricardo, N., Feitosa, J., & Muniz, E. (2012). Chitosan-graft- poly(acrylic acid)/rice husk ash based superabsorbent hydrogel composite: preparation and characterization. *Journal of Polymer Research*, 19(12).
- [37]. Rojas, O. J. (2016). *Cellulose Chemistry and Properties: Fibers, Nanocelluloses and Advanced Materials*. New York : Springer

- International Publishing.
- [38]. Sahoo, D., & Biswal, T. (2021). Alginate and its application to tissue engineering. *SN Applied Sciences*. doi:10.1007/s42452-020-04096-w.
- [39]. Sampath U., Ching, Y., Chuah, C., Singh, R., & Lin, P.-C. (2017). Preparation and characterization of nanocellulose reinforced semi-interpenetrating polymer network of chitosan hydrogel. *Cellulose*, 24(5), 2215-2228.
- [40]. Sarah Husnaini, Zainala Nurul, Hanisah Mohda, Nabilah Suhailia, Farah Hannan, Anuarab Azwan, Mat Lazimab, Rizafizah Othaman.,(2021). Preparation of cellulose-based hydrogel: a review. *Journal of Materials Research and Technology*.
- [41]. Sarmah, D., & Karak, N. (2020). Double network hydrophobic starch based amphoteric hydrogel as an effective adsorbent for both cationic and anionic dyes. *Carbohydrate Polymers*, 242. doi:10.1016/j.carbpol.2020.116320
- [42]. Stefan, D. S., Zainescu, G., Manea-Saghin, A.-M., Triantaphyllidou, I.-E., Tzoumani, I., I. Tatoulis, T., Meghea, A. (2020). Collagen-Based Hydrogels Composites from Hide Waste to Produce Smart Fertilizers. *MDPI*, 17.
- [43]. Subhan, H., Alam, S., Shah, L., Ali, M., & Farooq, M. (2021). Sodium alginate grafted poly(N-vinyl formamide-co-acrylic acid)-bentonite clay hybrid hydrogel for sorptive removal of methylene green from wastewater. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. doi:10.1016/j.colsurfa.
- [44]. Suhas, . G. (2016). Cellulose: A review as natural, modified and activated carbon adsorbent. *Bioresource Technology*, 216, 1066-1076. doi:http://dx.doi.org/10.1016/j.biortech.2016.05.106
- [45]. Tamás Fekete, J. B. (2017). Synthesis of carboxymethylcellulose/ starch superabsorbent hydrogels by gamma-irradiation. *Chemistry Central Journal*, 11-46. doi:10.1186/s13065-017-0273-5
- [46]. Tanan W., Panichpakdee, J., & Saengsuwan, S. (2018). Novel Biodegradable Hydrogel Based on Natural Polymers: Synthesis, characterization, Swelling/Reswelling and Biodegradability. *European Polymer Journal*.
- [47]. Thombare, N., Mishra, S., Siddiqui, M., Jha, U., Singh, D., & Mahajan, G. (2017). Design and development of guar gum based novel, superabsorbent and moistureretaining hydrogel for agricultural applications. *Carbohydrate polymers*, 26.
- [48]. Varaprasad, K., Reddy, N., Kumar, N., Vimala, K., Ravindra, S., & Raju, K. (2010). Poly(acrylamide- chitosan) Hydrogels: Interaction with Surfactants. *International Journal of Polymeric Materials*, 59(12), 981-993.
- [49]. Vudjung, C., Chaisuwan, U., Pangan, U., Chaipugdee, N., Boonyod, S., Santawitee, O., & Saengsuwan, S. (2014). Effect of Natural Rubber Contents on Biodegradation and Water Absorption of Interpenetrating Polymer Network (IPN) Hydrogel from Natural Rubber and Cassava Starch. *Energy Procedia*, 255–263.
- [50]. Wang, W., & Wang, A. (2010). Synthesis and swelling properties of pH-sensitive semi-IPN superabsorbent hydrogels based on sodium alginate-g-poly(sodium acrylate) and polyvinylpyrrolidone. *Carbohydrate Polymers*. doi:10.1016/j.carbpol.2010.01.020.
- [51]. Wei-Min Cheng, X.-M. H.-M.-H. (2015). Preparation and Characteristics of Corn Straw-Co-AMPS-Co-AA Superabsorbent Hydrogel. *Polymers*, 7, 2431–2445.
- [52]. Yin Wang, L. Y. (2020). A novel cellulose hydrogel coating with nanoscale Fe₀ for Cr(VI) adsorption and reduction. *Science of the Total Environment*.
- [53]. Yin Wang, L. Y. (2020). A novel cellulose hydrogel coating with nanoscale Fe₀ for Cr(VI) adsorption and reduction. *Science of the Total Environment*. doi:https://doi.org/10.1016/j.scitotenv.2020.138625
- [54]. Zhao, L., Mitomo, H., Zhai, M., Yoshii, F., Nagasawa, N., & Kume, T. (2003). Synthesis of antibacterial PVA/CM-chitosan blend hydrogels with electron beam irradiation. *Carbohydrate Polymers*, 53(4), 439-446.
- [55]. Zhoua, Y., Gua, Z., Liu, J., Huang, K., Liu, G., & Wu, J. (2019). Arginine based poly (ester amide)/ hyaluronic id hybrid hydrogels for bone tissues engineering. *Elsevier*, 11