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Synthesis of Hydrogel from Acrylic Acid

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Submitted by:

- Beribeche Kamel
- Beribeche Ali
- Beribeche Mokhtar

Before The Jury Composed of the Professor:

Dr. Boudouh Issam	**President**	University of El-Oued
Dr. Ben Seghir Bachir	**Examiner**	University of El-Oued
Pr. Ben Mya Omar	**Supervisor**	University of El-Oued

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Dedication

We dedicate this work to the dearest people and those closest to our hearts, our generous family that supported us and bore our burdens throughout our journey, and their blessed prayer which had an impact on completing this work.

To our professors who immersed us with appreciation, advice, and guidance.

To all of them we dedicate this humble work, asking Allah Almighty to benefit us with it, and grant us success.

Acknowledgement

Praise be to Allah for His generosity and grace that enabled us to complete this work. we hope that he will accept it from us and count it for us in the balance of our good deeds and balance of those who helped us to accomplish this work.

Our thanks go to the people who, directly or indirectly, provided us with guidance, advice or any kind of assistance in completing this study. in this context, we extend our sincere thanks and appreciation to our supervisor professor **Ben Mya Omar** for his academic sponsorship and the psychological and moral support.

We would like to thank our elite professors and members of the discussion committee and all the Process Engineering and Petro chemistry Department's members; teachers, students and staff for their spirit of cooperation. finally, we would like to Express our gratitude to all teachers who worked hard for us during our whole educational career.

Abstract

The problem of water consumption and water retention is one of the most important issues in irrigating agricultural crops in dry and desert areas. Research has suggested hydrogels, which are three-way coherent polymeric networks that have the ability to absorb liquids and retain them for a long time, due to their porous shape and water-repellent properties. In this study, acrylic acid super porous gels prepared using gas blowing (or foaming) technology were made to improve the water consumption process, and compared to the performance of commercial super absorbent hydrogels (potassium polyacrylic), polymerization led to a decrease in product quality and quantity due to the high concentration of the reactants, which slowed the polymerization process, as well as the drying method was not effective in this study due to the lack of reaction of the components of the production completely, and they remained fixed on the surface of the gel. These factors affected the polymerization, swell capacity test and surface porosity study, as well as the amount of water absorption and the speed of reaching swell equilibrium compared to the performance of commercial super-absorbent hydrogels.

Key words: hydrogels, super-porous and super-absorbent hydrogel, polymerization process, acrylic acid.

الملخص

مشكلة استهلاك المياه والاحتفاظ بها، هي قضية مهمة في ري المحاصيل الزراعية في المناطق الجافة والصحراوية. اقترحت الأبحاث هلاميات المائية، وهي شبكات بوليميرية ثلاثية الأبعاد متماسكة لديها القدرة على امتصاص السوائل والاحتفاظ بها لفترة طويلة، بسبب شكلها المسامي وخصائصها المقاومة للماء. في هذه الدراسة، تم تصنيع المواد الهلامية فائقة المسام بحمض الأكريليك المحضرة باستخدام تقنية نفخ الغاز (أو الرغوة) لتحسين عملية استهلاك المياه، ومقارنتها بأداء الهلاميات المائية التجارية فائقة الامتصاص (بولي أكريليك البوتاسيوم) .أدت البلمرة الى انخفاض في جودة وكمية المنتج بسبب التركيز العالي للمواد المتفاعلة التي تبطئ في عملية البلمرة، وكذلك طريقة التجفيف لم تكن فعالة في هذه الدراسة بسبب عدم تفاعل المواد المكونة لإنتاج بشكل كامل، وبقيت مترسبة على سطح من الهلام، اثرت هذه العوامل على عملية البلمرة واختبار سعة الانتفاخ ودراسة مسامية السطح، وكذلك كمية امتصاص الماء وسرعة وصول الى التوازن الانتفاخ مقارنة بأداء الهيدروجيل التجاري عالي الامتصاص.

الكلمات المفتاحية: هلاميات المائية، هيدروجيل فائق المسامية وفائق الامتصاص، عملية البلمرة، حمض الاكريليك.

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LIST of Abbreviations

PHEMA: polyhydroxyethylmethacrylate.

PEG-PLA: Poly (lactic acid)/poly (ethylene glycol).

IPN: Interpenetrating Network.

PVP: poly (vinyl pyrrolidone).

PLA: poly (lactic acid).

PEG: poly (ethylene glycol).

PVA: poly (vinyl alcohol).

PEG: polyethylene glycol.

SAPs: superabsorbent polymers.

SPHs: super porous hydrogels.

CMC: Carboxymethyl cellulose.

PEO–PPO–PEO: poly (ethylene oxide) / poly (propylene oxide) and poly (ethylene oxide).

W_s: Hydrogel weight in bulge.

W_d: weight of hydrogel in dry state.

C: Hydrogel in case of swelling.

B: Hydrogel in dry state.

Q: the swelling.

EM: Electron Microscopy.

FTIR: Fourier Transform Infrared Spectroscopy.

XRD: X-ray diffraction.

PAAm: poly (allyl amine).

AA: Acrylic acid.

EDTA: Ethylene diamine tetra-acetic acid.

General Introduction

There is a need for plant growth with increased water and nutrient holding capacity, as well as reduced watering frequency as they produce. Several studies have suggested that hydrogels can provide and extend the life and quality of crops, and they are also widely used in health, agricultural and horticultural products, and water-retaining materials, given the diversity of materials preparation methods and properties Hydrogels are cohesive and insoluble three-dimensional hydrophilic polymeric networks that have the ability to swell and remove swelling and retain large amounts of fluid in a swollen state due to the presence of pores in their external structure and properties to absorb fluids and retain them for a long time, and can biodegrade for a period depending on the type of polymer the factory.

The study dealt with the synthesis of hydrogel from acrylic acid by gas blowing technique (or foam) and this type is called super porous hydrogels due to its structure and its ability to improve water consumption for irrigation and compare its performance with commercial super absorbent hydrogels from the invention of hydrogels to the present day there has been a difference in the manufacture of hydrogels, and they can be made from many different monomers, either synthetic or natural. What are the classifications and applications of hydrogels? What are the techniques adopted in preparing the hydrogel and the means used in analyzing the product? How is the process of synthesis of hydrogels using gas or foam blowing technique?

Hydrogels can be classified according to the source of the monomer from which they are made, the method of preparation, their properties, their responses to external environmental conditions and their biodegradation. Hydrogels are used in many areas of life, due to their chemical composition and properties. There are several techniques in the synthesis of hydrogels, divided into two types, chemical techniques and physical techniques, and this diversity in the composition generates a difference in the composition, properties and external structure of the gel, and it is evident through several methods including infrared spectroscopy to discover the chemical composition of the gel, and diffraction of rays X-rays to give the structural composition, proportion and crystal dimension, in addition to optical microscopy and scanning electron to give information about the shape of the surface of the materials, and an image of the inner network of the gel.

Hydrogels are manufactured by gas blowing technology, a newer version, using a foaming agent during polymerization to produce bubbles, release gas, and form a pore shape on the gel structure.

In the first chapter, our study dealt with general information about hydrogels from the history of their appearance to their evolution through generations, as well as the classifications on the basis of which they were classified, their various characteristics, the external conditions affecting hydrogels, and the areas of their application in life.

In the second chapter, we discussed the types of physical and chemical synthesis techniques present in the fabrication and analysis methods for on-gel detection and study.

In the last chapter, we reviewed experimental work to describe the technology of acrylic acid hydrogel synthesis using gas blowing technique and to study some important properties. We also made a comparison with commercial potassium polyacrylic super absorbent hydrogels.

Chapter 01:

Generalities About Hydrogel

I-Introduction:

From the first hydrogels invention till nowadays, researchers have been defining hydrogels in many different ways, The most common definition is that hydrogel is a water-swollen, cross-linked polymeric network obtained industrially by a simple reaction of one or more monomers ,Hydrogels can be described as hydrophilic polymers which do not dissolve, but can swell in surrounding fluid [1] , swell to the extent, which is mainly determined by the hydrogel network crosslink density[2], which are capable of absorbing 400 times approximately or more of its weight in deionized water or 150–300 times its weight in irrigation water in most of the soil[3] , Hydrogel is widely used in life in agriculture, medicine in industry as preservative and water absorbent.

This chapter reviews generalities about hydrogel: - What is the history of the emergence and development of hydrogel?

- What are the types of hydrogel, their physical and chemical properties, the environmental conditions it is affected by and the field of application?

- What is the concept of agricultural hydrogel, its basic types, advantages and disadvantages in agriculture?

I-1-History of The Emergence and Development of Hydrogel:

The word “hydrogel”, according to Lee, Kwon and Park, dates back toan article published in 1894. Anyway, the material described there was not a hydrogel as we describe it today; it was indeed a colloidal gel made with inorganic salts. Is yet remarkable to notice how the history of the term itself is consistently long. Anyhow, the first cross-linked network material that appeared in literature and has been described by its typical hydrogel properties, one for all the high water affinity, was a polyhydroxyethylmethacrylate (PHEMA) hydrogel developed much later, in 1960, with the ambitious goal of using them in permanent contact applications with human tissues, hydrogels are in investigation and development of stereo complexed materials (e.g. PEG-PLA interaction) hydrogels cross linked by other physical interactions (e.g. cyclodextrines) . This progress in hydrogel’s science is quickly leading to an increasing interest in the development of the so called “smart hydrogels”, polymeric matrixes with a wide spectrum of tunable properties and trigger stimuli. The topic is theoretically inexhaustible and the possible applications, the engineering and medical devices that can be obtained from it are above any imagination. Since the pioneering work of Wichterle and Lim in 1960 on cross-linked hydrogels, and because of their hydrophilic

character and potential to be biocompatible, hydrogels have been of great interest to biomaterial scientists for many years. The important and influential work of Lim and Sun in 1980 demonstrated the successful application of calcium alginate microcapsules for cell encapsulation. Later in the 1980s, Yannas and coworkers incorporated natural polymers such as collagen and shark cartilage into hydrogels for use as artificial burn dressings. Hydrogels based on both natural and synthetic polymers have continued to be of interest for encapsulation of cells and most recently such hydrogels have become especially attractive to the new field of "tissue engineering" as matrices for repairing and regenerating a wide variety of tissues and organs fact the first materials developed for uses inside the patient. Since then the number of studies about hydrogels for biomedical applications began to rise, especially from the decade of 70's. The aims and goals and the number of materials changed and enlarged constantly over the years. As suggested by Buwalda et al., the history of hydrogels can be divided in three main blocks. A hydrogel's first generation that comprises a wide range of crosslinking procedures involving the chemical modifications of a monomer or polymer with an initiator. The general aim is to develop material with high swelling, good mechanical properties and relatively simple rationale. Then, starting in the seventies, a different concept of hydrogel grew in importance: a second generation of materials capable of a response to specific stimuli, such as variations in temperature, pH or concentration of specific molecules in solution. These specific stimuli can be exploited to trigger likewise specific events, for example the polymerization of the material, a drug delivery or an in situ pore formation. Finally, a third generation of hydrogels focusing on the investigation and development of stereo complexed materials (e.g. PEG-PLA interaction) hydrogels cross linked by other physical interactions (e.g. cyclodextrines). This progress in hydrogel's science is quickly leading to an increasing interest in the development of the so called "smart hydrogels", polymeric matrixes with a wide spectrum of tunable properties and trigger stimuli. The topic is theoretically inexhaustible and the possible applications, the engineering and medical devices that can be obtained from it are above any imagination. Since the pioneering work of Wichterle and Lim in 1960 on cross-linked hydrogels, and because of their hydrophilic character and potential to be biocompatible, hydrogels have been of great interest to biomaterial scientists for many years. The important and influential work of Lim and Sun in 1980. Demonstrated the successful application of calcium alginate microcapsules for cell encapsulation. Later in the 1980s, Yannas and coworkers incorporated natural polymers such as collagen and shark cartilage into hydrogels for use as artificial burn dressings. Hydrogels based on both natural and synthetic polymers have continued to be of interest for

encapsulation of cells and most recently such hydrogels have become especially attractive to the new field of "tissue engineering" as matrices for repairing and regenerating a wide variety of tissues and organs [4].

I-2-Classification of Hydrogels:

There is a diversity in the classification of hydrogels according to several criteria and in figure (01) a classification is based on the source of the material, method of preparation, physical properties, ionic charges, crosslinking, biological decomposition and response:

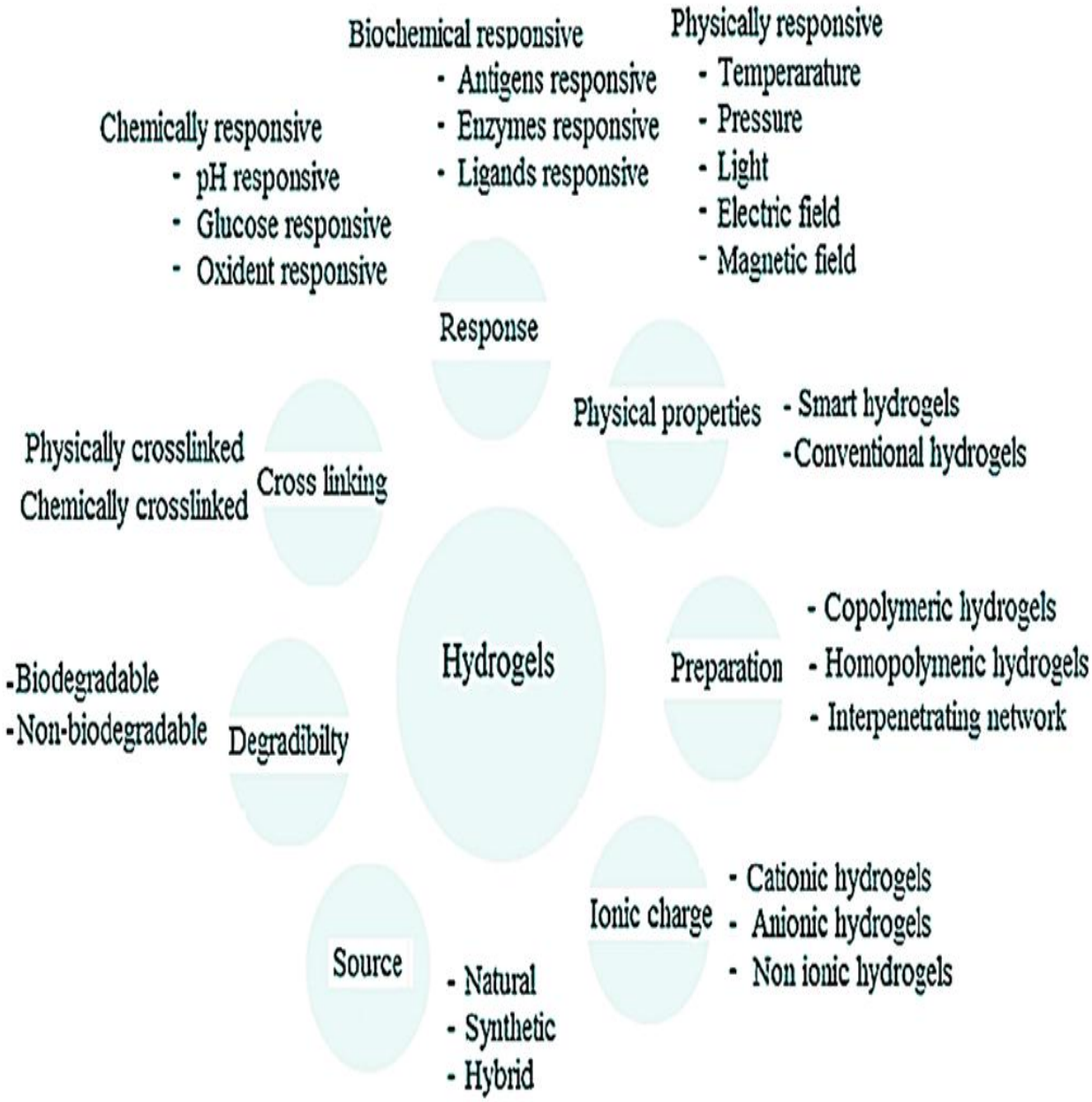


Figure01: Classification of hydrogels based on the different properties [5]**.**

I-2-1-Classification Based On Source:

- Natural Hydrogels:

Natural hydrogels are of natural origin and are prepared using natural polymers such as proteins and polysaccharides like alginate, chitosan and dextran [6].

- Synthetic Hydrogels:

Synthetic hydrogels are of synthetic origin and are synthesized via chemical polymerization using man-made monomers. These hydrogels can be homopolymeric, copolymeric and multipolymeric. Poly (ethylene glycol)–polylactide-poly (ethylene glycol)-based hydrogel is an example of a synthetic hydrogel [6]**.**

- Hybrid Hydrogels:

Hybrid hydrogels are prepared by combining natural polymers with synthetic polymers. Wang et al. synthesized a protein cross-linked 2-hydroxypropyl meth acrylamide hybrid hydrogel [6].

I-2-2-Classification Based On Preparation:

- Homopolymer Hydrogels:

Homopolymer hydrogels are cross-linked polymer networks derived from one type of monomer. The structural framework of these hydrogels is dependent on the nature of the monomer, polymerization technique and cross-linker. Polyethylene glycol-based hydrogel is an example of a homopolymer hydrogel, which is suitable for controlled release of drugs, biomolecules and protein and is widely used in drug delivery systems [6].

- Copolymer Hydrogels**:**

Copolymer hydrogels are produced from two types of monomer where one of the monomers is hydrophilic and responsible for the swell ability of the hydrogel. These are arranged in a different configuration like graft, random, block and alternate type. These hydrogels are chemically synthesized by polymerization or cross-linking of both monomers using an initiator and a cross-linker. These can also be physically cross-linked by different forces, namely chain aggregations, hydrogen bonding, ionic interaction and ion-polymer complexations. Carboxymethyl cellulose and carboxymethyl chitosan-based hydrogels, which are used for the adsorption of metal ion are examples of copolymer hydrogels [6].

- Interpenetrating Network (IPN):

Interpenetrating network is an important class of hydrogels, made up of two intertwined polymer networks without any chemical bond between the polymers. The network of the first polymer is linear, whereas the second polymer has a cross-linked network. The linear network of the first polymer diffuses into the second polymer. Acrylamide/acrylic acid copolymer hydrogels containing polyallylammonium chloride, which is used for the release of theophylline is an example of a semi-interpenetrating network. This interpenetrating hydrogel is pH sensitive, and N, N′-methylenebisacrylamide was used as a cross-linker to synthesize this hydrogel [6].

I-2-3-Classification Based on Ionic Charge:

Hydrogels are classified into three groups on the basis of nature of electric charge on the cross-linked chains:

- Non-Ionic Hydrogels:

Neutral hydrogels carry no charge on their backbone or side groups [6].

- Cationic hydrogels:

Cationic hydrogels containing positively charged groups (e.g. amines and sulphonic acid) and exhibit an increase in the swelling at low pH [6].

- Anionic hydrogels:

Anionic hydrogels containing negatively charged groups (carboxylic acid, sulphonic acid) and show an increase in swelling at high pH [6].

I-2-4-Classification Based on Cross-Linking:

On the basis of nature of cross-linking, hydrogels are of two types:

- Chemically Cross-Linked Hydrogels:

In chemically cross-linked hydrogels, covalent bonds exist between different polymer chains. Therefore, they are stable and cannot be dissolved in any solvents unless the covalent crosslink points are cleaved. The design flexibility of a physically cross-linked hydrogel is restricted, due to the difficulty in decoupling the variables, such as: gelation time, internal network pore size, chemical functionalization and degradation time. In contrast, chemical cross-linking results in a network with a relatively high mechanical strength and depending on

the type of the chemical bonds in the building blocks and the crosslinks, relatively extended degradation times can occur [7].

- Physically cross-linked:

Physically cross-linked hydrogels or reversible gels have gained significance due to their relative ease of production and the advantage of not using cross-linking agents during their synthesis protocol. Dissolution of physically cross-linked gels is prevented by physical interactions, which exist between different polymer chains. The selection of hydrocolloid type depends on concentration and pH can lead to the formation of a broad variety of gel textures and is currently an area receiving considerable attention, in the food, pharmaceutical and biomedical applications because the use of cross-linking agents is generally avoided [7].

I-2-5-Classification Based On Physical Properties:

- Smart hydrogel:

Smart hydrogel systems with various chemically and structurally responsive moieties exhibit responsiveness to external stimuli including temperature, pH, ionic concentration, light, magnetic fields, electrical fields and chemicals. Polymers with multiple responsive properties have also been developed elegantly combining two or more stimuli-responsive mechanisms. Smart polymer hydrogels change their structural and volume phase transition as a response to external stimuli resulting in an enormous potential for scientific observations and for various advanced technological application [8].

- Conventional hydrogels:

Conventional hydrogels change little in swelling with environmental conditions while stimuli-responsive hydrogels may swell or Deswell sharply with relatively small changes of temperature or pH. [9].

I-2-6-Classification Based On Degradability:

- Biodegradable:

These are those polymers which get decomposed under aerobic or anaerobic conditions, as a result of the action of microorganism/enzymes. The materials develop it like starch, cellulose, and polyesters. Aliphatic polyesters are the most commonly used polymers [10].

- Non-Biodegradable:

They consist of long chains of carbon and hydrogen atoms. These molecules form an interatomic type of bonding and is adamant meaning it is tough for microbes to break the bonds and digest them. Thus a long period is required to decompose them [10].

I-2-7-Classification Based on Response [5]:

- Chemically responsive:

-pH responsive

-*glucose res*ponsive

-oxidant responsive

- Biochemical responsive:

-Antigens responsive

-Enzymes responsive

-ligands responsive

- Physically responsive:

-Temperature

-pressure

-light

-Electric field

-Magnetic field

I-3-Hydrogel Properties:

The properties of the super absorbent hydrogel polymers are given below:

- High water absorption capacity;

- Different water absorbing rate depending on the required application;

- Colorless, odorless and non-toxic;

- High water absorbency under load;

- Re-swelling capacity;

- Biodegradability;

-Biocompatibility;

-Good durability and stability in swelling environment [11].

-hydrogel composition retains moisture and additive properties;

-It has a positive effect on the structure of the soil;

-prevents the appearance of cracks on the surface of the soil;

-Shelf life is long in the soil (about 5 years) [10].

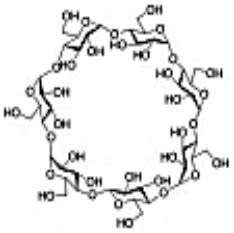
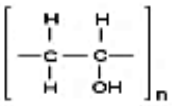
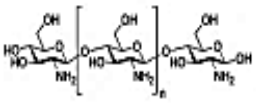
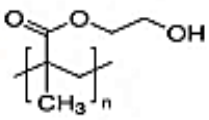
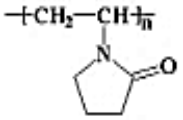
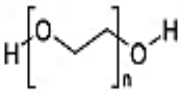
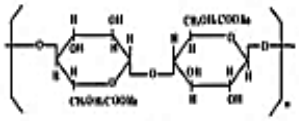
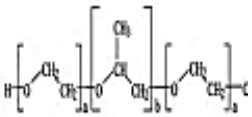
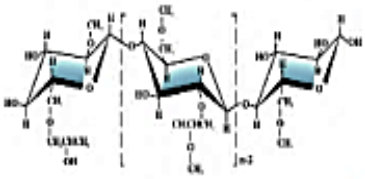
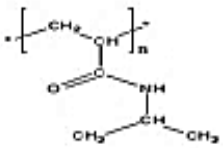
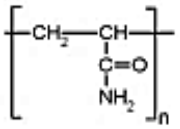
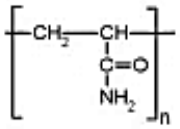
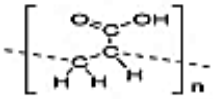
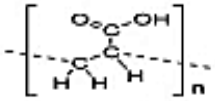
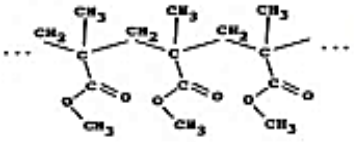
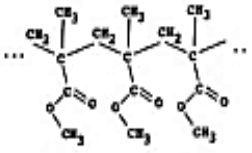
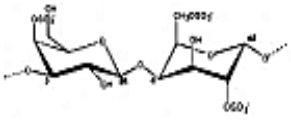
-Represents the characteristic property of hydrogels, in general, they can swell by 10-98% relative to their weight, depending on the pH, temperature or in the presence of ionic forces [12].

I-4-Composition of Hydrogels:

Cross-linked polymers are known as hydrogels regardless of whether they are synthetic grafted polymer derivatives or natural and/or a combination of both. Hydrogels comprising of naturally occurring polymers are called natural hydrogels, owing to the characteristic of non-toxicity, and are exuberantly marketed at cheap prices. Natural polymers can be classified into various categories depending upon their chemical structure. These belong to a variety of classes based on their chemical structure: (1) polysaccharides (chitin, chitosan, cellulose, starch, gums, alginate, and carrageenan), (2) biological polymers (nucleic acid and DNA), (3) polyamides (collagen), (4) polyphenols (lignin), (5) organic polyesters, (6) inorganic polyesters (polyphosphazene), and (7) polyanhydrides (poly sebacic acid). Hydrogels formed from naturally occurring polymers, especially polysaccharides and proteins, are similar to extracellular matrix due to their natural origin and can easily be identified by the cells and, hence, appear to be biocompatible. Nevertheless, hydrogels synthesized from natural polymers, specifically chitosan and other polysaccharides, are delicate. In order to improve their mechanical properties, natural polymers are cross-linked, grafted with monomers, or blended with synthetic polymers. For example, synthetic polymer poly (vinyl alcohol) is used as a blending agent to increase the mechanical strength and flexibility of natural polymers. Synthetic hydrogels contain synthetic polymers which offer more flexibility to tune the mechanical properties of the hydrogel. The most commonly used synthetic polymers are

polycaprolactone, poly (vinyl pyrrolidone) (PVP), poly (lactic acid) (PLA), poly (ethylene glycol) (PEG), and poly (vinyl alcohol) (PVA). PEG is water-soluble, biocompatible, and biodegradable and is especially important as it can conjugate with peptides, proteins, and some other drugs. PEG is also utilized to graft with some natural polymers to induce typical properties required for specific application. Bhattarai et al. synthesized PEG-graft-chitosan as injectable thermo responsive hydrogels that are liquid at low temperatures but solidify at room temperature. [13]. Examples of some polymer used in hydrogel manufacturing.

Table 01: Polymers Used in Fabrication of Hydrogel Micro particles [14].

Polymer	Abbreviation	Chemical Structure	Polymer	Abbreviation	Chemical Structure
β-Cyclodextrin	β -CD		Polyvinyl alcohol	PVA	
Chitosan	CHIT		Polyhydroxy ethyl methacrylate	PHEMA	
Polyvinyl pyrollidone	PVP		Polyethylene glycol	PEG	
Carboxy methyl cellulose	CMC		Pluronic F127	PF127	
Hydroxy methyl cellulose	HMC		Poly (*N*-isopropylacrylamide)	PNIPAM	
Polyacrylamide	PAAm		Polyacrylamide	PAAm	
Polyacrylic acid	PAA		Polyacrylic acid	PAA	
Poly (methyl methacrylate)	PMMA		Poly (methyl methacrylate)	PMMA	
Carrageenan	CGN				

I-5-Environmental Conditions Affected by The Hydrogel:

Hydrogels are cohesive three-dimensional hydrophilic polymer networks that have the ability to swell or de-swell and retain a large amount of fluid in a swollen state. Contraction or expansion can be controlled by changes in external environmental conditions. There is a group of stimuli that the hydrogels are sensitive to, and they significantly change the size of the response. Due to their responsive properties to changes in temperature, electric or magnetic field, light, pressure and sound, pH, ionic strength of the surrounding medium, solvent composition, and molecular species that lead to changes in the hydrogel from a non-swollen to a swollen state. These catalysts are divided into two categories: physical catalysts and chemical catalysts, as shown in Figure (02). Swelling and contraction in response to changes in the external environment of synthetic hydrogels has been an area of research by researchers over the decades and is still active today [1,15-17].

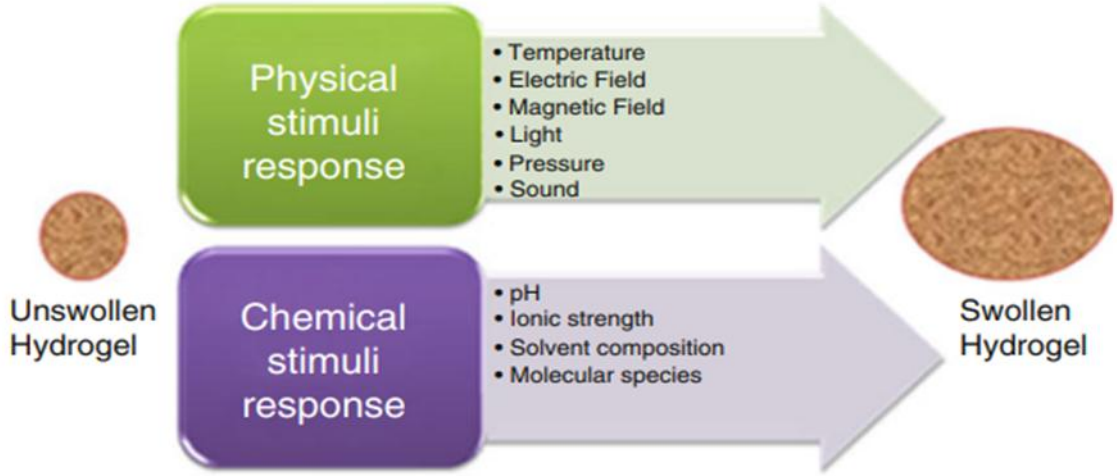


Figure02: Schematic representation of stimuli-responsive hydrogel [17]**.**

I-6-Applications Hydrogel:

Hydrogel has many uses in life as shown in Figure (03):

I-6-1-Agriculture Application:

Superabsorbent hydrogels used in agriculture. Can reduce water consumption, improve fertilizer retention in soil and lower death rate of plants and increase plant growth [18].

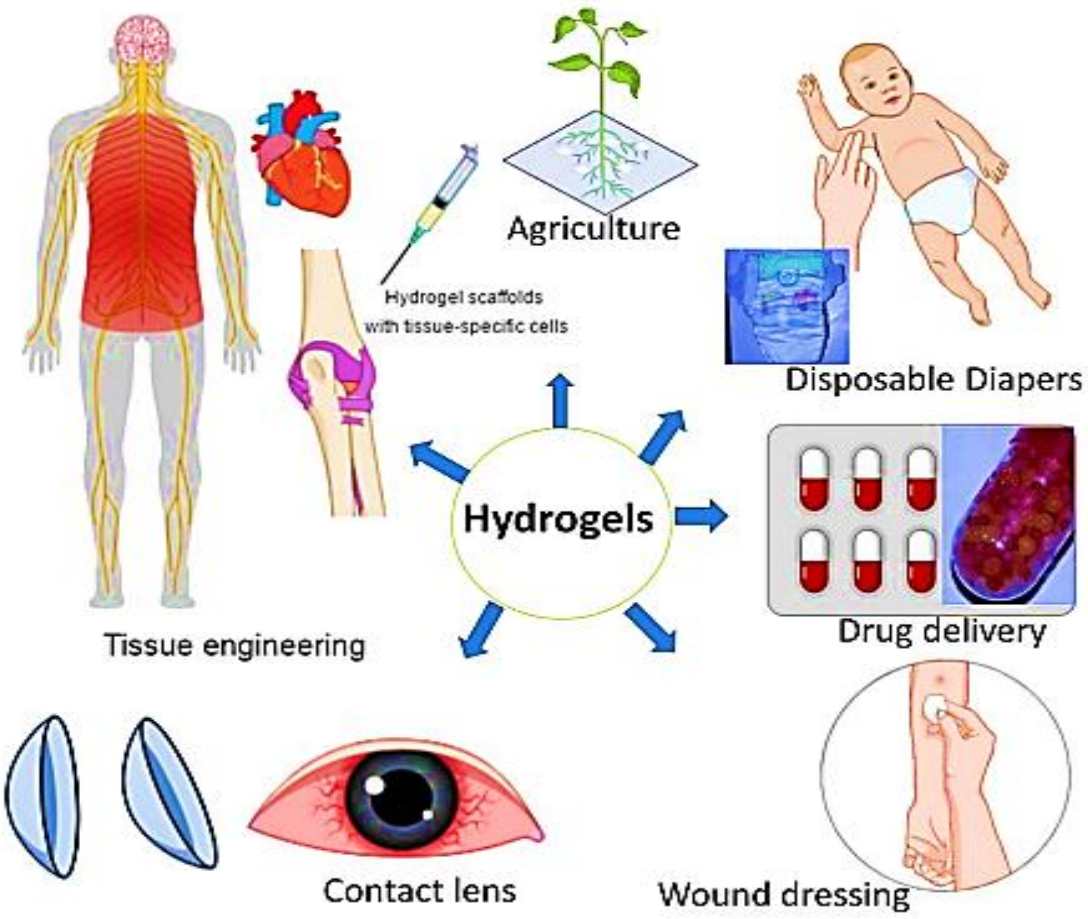


Figure03: Applications hydrogel. [18]

I-6-2-Biomedical Application:

Biomedical Application Hydrogels are widely used in biomedical applications such as, in Immunotherapy, Vaccine, Plastic surgery, wound healing, Proteomic, Tissue engineering (Bone regeneration, Cardiac, Dental), Drug delivery, Wound dressing and so on [16].

I-6-3-Environmental Applications:

Environmental applications different types of hydrogels are used for waste water treatment that can hold a lot of microorganism in their matrix. Currently, the biggest environmental problem is the loss of oil in seas or in other water sources. Many researchers and authors attempted to develop different types of hydrogels to retain water with oil-pollutant molecules [16] .

I-6-4-Cosmetics Applications:

Contact Lenses It is the most widely used application of this polymer for soft contact lenses, poly (2-hydroxyethyl methacrylate)-based hydrogels are used due to their extensive property [16].

I-6-5-Industrial Applications:

Hygienic products – SAPs are widely used for absorbing water and aqueous solutions for baby diapers, adult incontinence products and feminine hygiene products. This application of SAPs replaces traditional absorbing materials such as cotton, cloth, paper etc., which has some drawbacks like low efficiency, low recyclability, and leakage. Cellulose based hydrogels have been mostly used for this application [11].

I-7-Hydrogels for Agriculture:

I-7-1-Hydrogels for Agriculture:

SAPS are white sugar - like hygroscopic materials that swell in water to form a clear gel made of separate individual particles and which can retain moisture even under pressure without risk of conflagration or rupturing / blasting. Super Absorbent Polymers used in agriculture are made from acrylic acids and a cross-linking agent like potassium by solution or suspension polymerization. The polymer produced is called a polyacrylate. The swelling capacity and gel modulus depend greatly on the quantity and type of cross-linker used. Polyacrylates polymers are non-toxic, non-irritating and non-corrosive in nature and tested to be biodegradable with a degradation rate of 10%-15% per year. These polymers show high water absorbent potential and can freely release 95% water of the same under suction pressure by plant roots [19].

The following Figures (04) show hydrogels for cultivation:

Figures04: Hydrogels of Agriculture [20,21]**.**

I-7-2-Key Characteristics of Hydrogels in Agriculture:

▪ Hydrogels are less affected by the presence of salts in the soil;

▪ They improve the physical properties of soils and restores its biota;

▪ They promote the seed germination rate and the rate of seedling emergence;

▪ They can improve root growth and plant density;

▪ They relieve the plants from moisture stress and make them to withstand prolonged moisture stress;

▪ They reduce nursery establishment period;

▪ They reduce the irrigation frequencies and fertilization requirements of crops with improved input use efficiency [19].

I-7-3-Types of Hydrogels for Agriculture:

Hydrogels are also known as cross linked three - dimensional networked water absorbent polymers. There are mainly three types of Hydrogels for agricultural use:

▪ Starch - graft copolymers.

▪ Cross - linked Polyacrylates.

▪ Cross - linked Polyacrylamides & Acrylamide - acrylate copolymers.

Potassium Polyacrylate is the major element used in Hydrogel technology and marketed as Hydrogel for agricultural. This is mainly used for its capability for longer periods of water retention and high efficiency in soil with absolutely no toxicity issues [19].

I-7-4-Advantages and Disadvantages of Hydrogel in Agriculture:

I-7-4-1-Advantages of Hydrogel in Agriculture**:**

-Improving the physical, chemical and biological properties of the soil;

-Helps to save irrigation water;

-Agricultural hydrogels are environmentally friendly because they are biodegradable;

-Hydrogels are non-toxic;

- Helps to increase agricultural production with sustainability in the environment and water stress;

- Hydrogels provide space for soil aeration and improvement [22].

-It acts as a temperature regulator for the roots of the plant;

-The development of plant production in interesting climatic regions;

-Improves plant resistance to diseases;

-Amplifies the growth of root and leaf masses by 3 to 5 times [23].

I-7-4-2-Disadvantages of Hydrogel in Agriculture**:**

-Hydrogels significantly reduce their water absorption if there are any ions in the water, soil or fertilizers used in agriculture;

-The cost of the hydrogel is so high that it is only used in agricultural crops of great value;

-Hydrogel alone cannot be relied upon for a long time if there is not enough water or moisture in the soil [19].

I-Conclusion:

This chapter presents a general review of hydrogels since their inception and evolution through generations, the classification of hydrogels according to their different sources, physical, and chemical properties, methods of preparation and analysis. The fields of application in life and external environmental conditions affected by the gels. The study also describes agricultural hydrogels, their basic characteristics and types, and advantages and disadvantages in agricultural.

Efforts are underway in the industry for the provision of new types of hydrogels, and this leads to a difference in preparation methods.

Chapter 02:

General Methods of Preparation and Analysis

II-Introduction:

Hydrogels can be made from many different monomers, synthetic or natural (biological). The basis of the synthesis is acrylic acid or acrylamide [24]. Over the years, researchers have defined gels in several different ways [15] There are three classes of hydrogel structures. non-porous hydrogels; super absorbent hydrogels and ultra- porous hydrogels; These generations are prepared in several different ways, as well as differing in drying [24]. Hydrogels are studied by several analytical methods.

Newer versions of hydrogels can usually be made using gas blowing or foaming with a thinner and foam retardant in order to prepare ultra-absorbent and ultra-porous hydrogels [24], and are used in agriculture to improve dry soils and reduce irrigation water consumption.

In this study, we refer to the different methods of physical chemical preparation and analysis possibilities. So what are the techniques adopted in preparing the hydrogel? What are the methods and means used in the analysis?

II-1-Techniques Adopted in The Preparation of Hydrogel:

Hydrogels are usually prepared from polar monomers and can be divided according to the starting materials into natural polymer hydrogels, synthetic polymer hydrogels and groups of the two classes [25]. Hydrogels are polymer networks with hydrophilic properties, while hydrogels are generally prepared on hydrophobic monomers, sometimes in hydrogel preparations to regulate properties for specific applications [15]. In other words, a hydrogel is simply a hydrophilic polymeric network that is interconnected in some way to produce a flexible structure. Thus, any technology It is used to create a cross-linked polymer that can be used to produce hydrogel. It is produced from several monomers and acrylic acid Various synthetic methods are used for synthesis Super absorbent polymers. In general, can They are classified into two types: Chemical synthesis methods and physical methods. Chemical synthesis methods in Bulk polymerization, solution polymerization/crosslinking, suspension polymerization, reverse suspension polymerization and irradiation polymerization, And Physical methods refer: Heating/Cooling, Ionic Interaction, Complex Coacervation and Hydrogen Bonding. [26].

II-1-1-Chemical Synthesis Methods:

Chemical synthesis methods are widely used in the preparation of superabsorbent polymers, and we mention them in detail below:

II-1-1-1-Bulk polymerization:

Bulk polymerization, is also known as mass polymerization [24], is the simplest technique which involves only monomer and monomer-soluble initiators, As in Figure (05). High rate of polymerization and degree of polymerization occur because of the high concentration of monomer. However, the viscosity of reaction increases markedly with the conversion which generates the heat during polymerization [15]. These problems can be avoided by using the lower temperature and low concentration of initiators in the case of producing a lot of heat [24]. The bulk polymerization of monomers to make a homogeneous hydrogel produces a glassy, transparent polymer matrix which is very hard when immersed in water, the glassy matrix swells to become soft and flexible [15]. The advantage of bulk polymerization is that it produces high molecular weight polymer with high purity without complex devices [24].

Examples of Bulk Polymerization:

Poly (2-hydroxyethyl methacrylate) and poly (-acrylic acid) SAPs are prepared by these techniques [24].

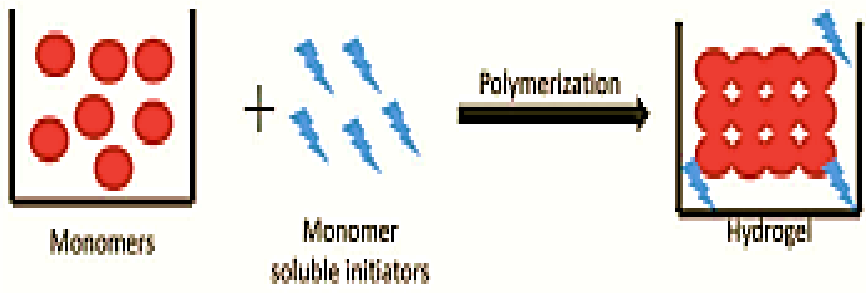


Figure 05: Preparation of hydrogel by bulk polymerization technique [27].

II-1-1-2-Solution Polymerization/Cross-Linking*:*

The solution polymerization reaction is an important method in the synthesis of polymers [24]. In the copolymerization/crosslinking reactions, the ionic or neutral monomers are mixed with the multifunctional crosslinking agent. Thermal polymerization is initiated by UV or redox initiator system. The presence of a solvent that acts as a heat sink is the main advantage of solution polymerization over bulk polymerization. Prepared hydrogels should be washed with distilled water to remove monomers, cross-linking agent, initiator, soluble and extractable polymer, and other impurities as shown in Figure (06). Typical solvents used for solution polymerization of hydrogels include water, ethanol, water-ethanol mixtures, and benzyl alcohol. The synthesis solvent can then be removed after which a gel is formed by

swelling of the hydrogels in water [15]. If the resulting polymers are water soluble, then it is called homogeneous solution polymerization; Drop-off polymerization occurs when polymers do not dissolve in water, we also call it heterogeneous polymerization. The best example is the preparation: poly (2-hydroxyethyl methacrylate) (PHEMA) [24].

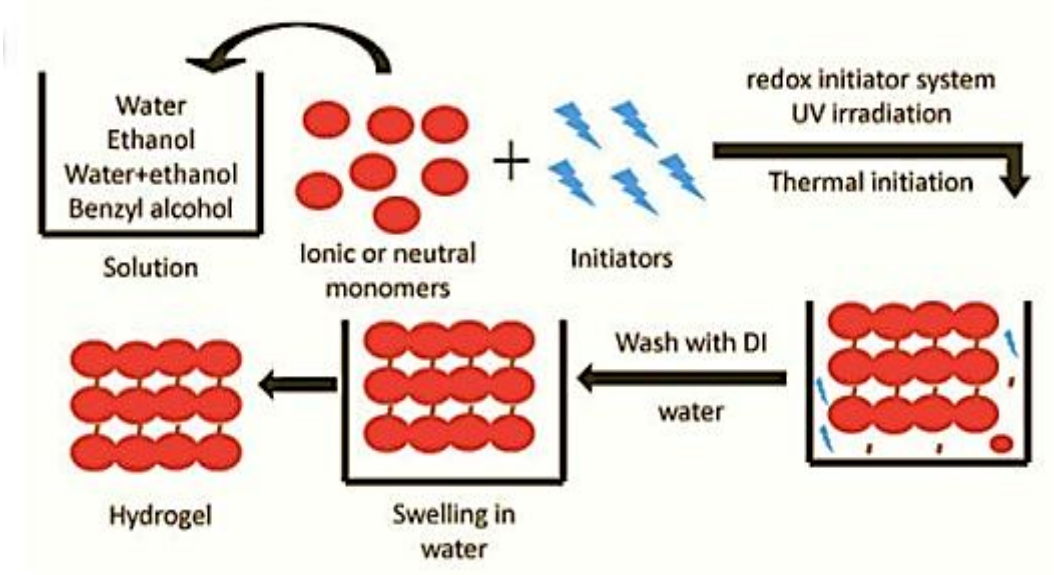


Figure 06: Preparation of hydrogel by solution technique [27].

II-1-1-3-Suspension Polymerization or Inverse-Suspension Polymerization:

Suspension polymerization or dispersion polymerization is a useful method since the products are obtained as powder or microscopic pellets (beads) [15], their micro-superabsorbent particles ranging in size from 1 μm to 1 mm. Suspension polymerization, the initiators are dissolved in water to form a droplet shape and radical-initiated polymerization is generated from thermal decomposition of the initiator. The suspension mechanism is similar to bulk polymerization [24]. The polymerization is referred to as "reversal." In this technique, the monomers and the initiator are dispersed. In the hydrocarbon phase as a homogeneous mixture. Monomer solution viscosity, agitation speed, rotor design، the type of dispersion mainly controls the size and shape of the resin particles [15]. This polymerization technique is illustrated in Figure (07).

Synthesis of SAP superabsorbent polymers by inverted suspension polymerization used corn starch, acrylic acid and crude acrylamide, cycloxane as continuous phase, N, N'-methylenebisacrylamide as cross-linking agent, potassium persulfate as initiator. In this way, fine particles of poly (hydroxyethyl methacrylate) were prepared [24].

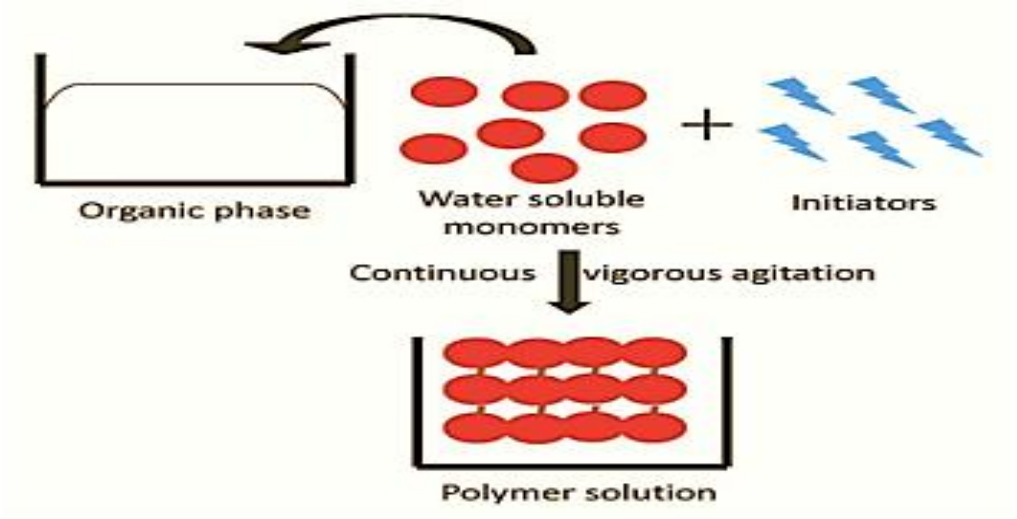


Figure 07: Preparation of hydrogel by Suspension or inverse-suspension [27].

II-1-1-4- Radiation Polymerization*:*

The irradiation polymerization technique was used for the first time in the polymerization of liquid ethylene [24]. High-energy ionizing radiation such as gamma rays, electron beams have been used as the initiator of polymerization to prepare hydrogels of unsaturated compounds. Irradiation of a water polymer solution results in the formation of radicals on the polymer chains. Also, the radiolysis of water molecules results in the formation of hydroxyl radicals, which also attack polymer chains, leading to their formation from large radicals [15]. Radiation vaccination is beneficial because it requires less time than chemical vaccination and thus prevents waste of time. Overall, easy technology, no starting units or cross-links, no waste, and relatively low operating costs [24]. The main advantage of irradiation initiating over chemical initiating is the production of relatively pure hydrogels and free of initiator. This technique is used in the production of cross-linked super absorbent polymers (SAP) such as poly (vinyl alcohol), poly (ethylene glycol), and poly (acrylic acid) [15]. The general mechanism of the synthesis of these polymers is as shown in the following Figure (08):

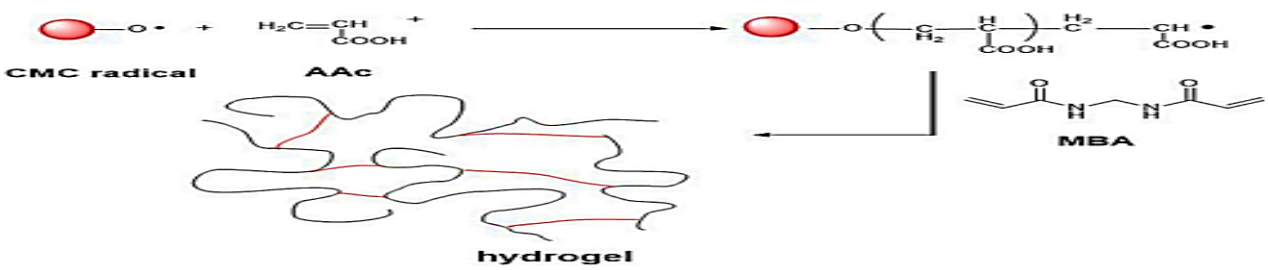


Figure 08: General mechanism for the radical cross-linking of CMC/AAc mixture in the presence of MBA [26].

II-1-1-5-Grafting*:*

Grafting involves the polymerization of a monomer onto the backbone of the preformed polymer. The polymer chains are activated by chemical reagents or high-energy radiation, which leads to infinite branching and cross-linking as shown in Figure (09). There are two types of grafting: Chemical grafting The molecular backbone is activated by the action of a chemical reagent. An example of this type is starch grafted with acrylic acid using N-Vinyl - 2-pyrolideme. As for the second type, radiation vaccination is activated by using high-energy radiation such as gamma and electron. An example is the preparation of a hydrogel for CMC by grafting the CMC with acrylic acid and activated by electron radiation in an aqueous solution [28,29].

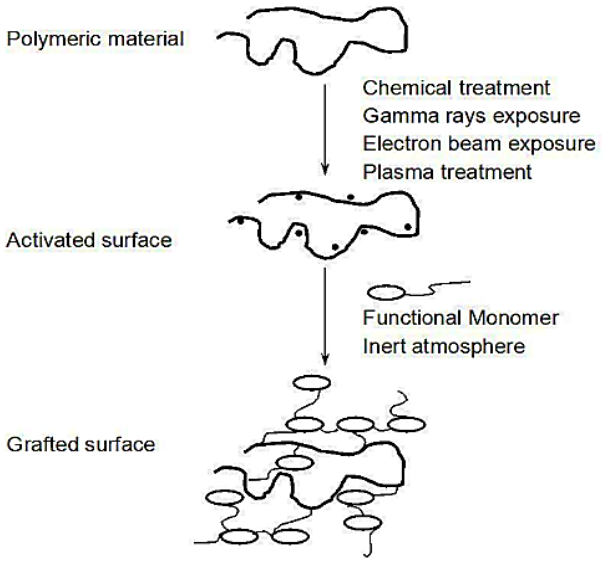


Figure 09: Grafting of a monomer on preformed polymeric backbone leading to infinite branching and cross-linking [28].

II-1-2-Physical Synthesis Methods:

Physical synthesis methods are molecular assembly by hydrogen cross bonds or ionic bonds between them polymers. Super absorbent polymers can be prepared at lower temperatures, unlike methods used at ambient temperatures. Poly super absorbent polymers are combined by a strong hydrogen bond. The different methods used to prepare the physical cross-linked gels are:

II-1-2-1-Heating/Cooling*:*

Physically cross-linked gels are formed when cooling hot solutions of gelatine or carrageenan. The gel formation is due to helix-formation, association of the helices, and

forming junction zones. Carrageenan in hot solution above the melting transition temperature is present as random coil conformation. Upon cooling it transforms to rigid helical rods [28], as in the figure (10). Some of the examples are polyethylene glycol polylactic acid hydrogel and polyethylene oxide-polypropylene oxide [30].

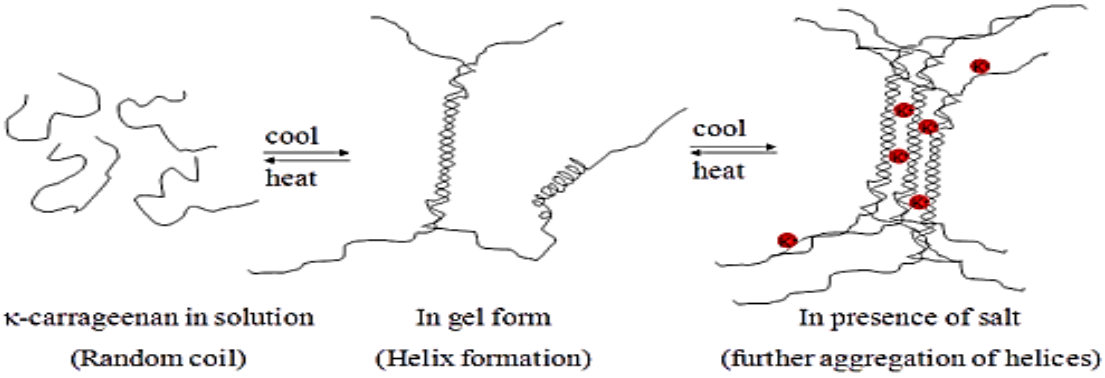


Figure (10): Gel formation due to aggregation of helix upon cooling a hot solution of carrageenan [29].

II-1-2-2-Ionic Interaction:

Ionic polymers cross-linked by the addition of di- or tri-valent counter ions result in hydrogel systems that fall in this category, this method underlies the principle of gelling a polyelectrolyte solution (e.g. $Na^{+}\ alginate^{-}$) with a multivalent ion of opposite charges (e.g. $Ca^{+2}\ +\ 2Cl^{-}$), Figure (11). Some other examples are chitosan-polyline, chitosan glycerol phosphate salt, chitosan-dextran hydrogels [29].

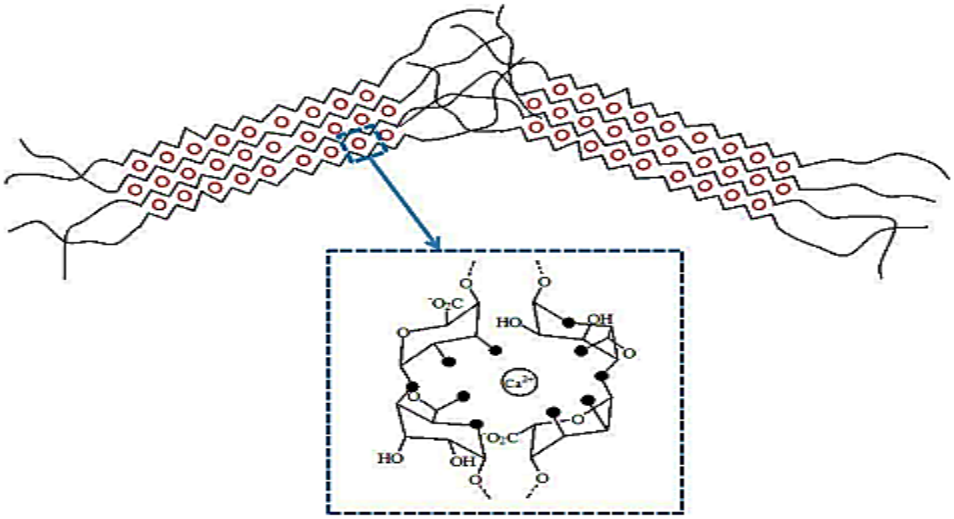


Figure 11: Inotropic gelation by interaction between anionic groups on alginate (COO^{-}) with divalent metal ions (Ca^{+2}) [29].

II-1-2-3-Complex Coacervation:

Formation of complex coacervate gels by mixing of polyanions with a polycations. The underlying principle of this method is that polymers with opposite charges stick together and form soluble and insoluble complexes depending on the concentration and pH of the respective solutions Figure (12). One such example is coacervating polyanionic xanthan with polycationic chitosan [29].

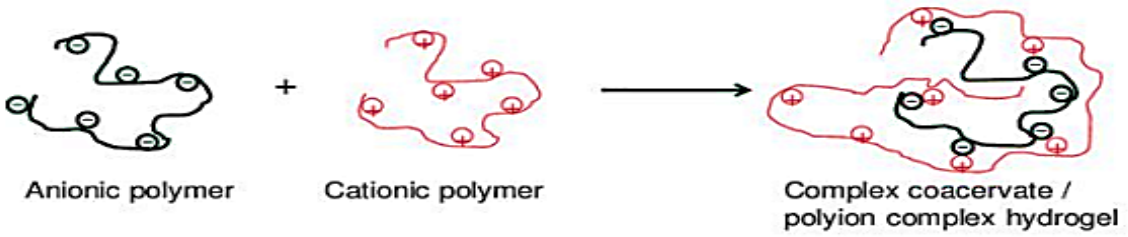


Figure 12: Complex coacervation between a polyanion and a polycation [29]**.**

II-1-2-4-Hydrogen Bonding:

Physically cross-linked gel-like structures can be prepared via hydrogen bonding interactions a hydrogen bond is formed through the association of electron deficient hydrogen atom and a functional group of high electron density [42]. An example of such hydrogel is a hydrogen-bound CMC (carboxymethyl cellulose) network formed by dispersing CMC into 0.1M HCl. The mechanism involves replacing the sodium in CMC with hydrogen in the acid solution to promote hydrogen bonding Figure (13) [29].

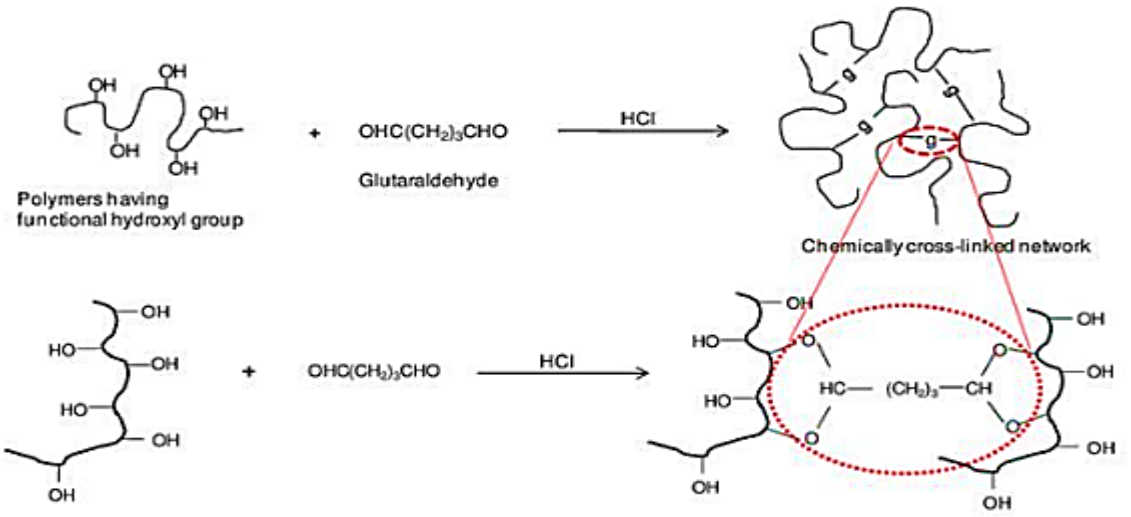


Figure 13: Schematic illustration of using chemical cross-linker to obtain cross-linked hydrogel network [29].

II-2-Preparation of Super Absorbent and Super Porous Hydrogels:

Super absorbent and porous hydrogels are cross-linked polymers that have the ability to absorb large amounts of water or liquids (10-1000 times their original weight or volume) in a short period of time. Hydrogels are prepared using several techniques, and modern SAPs and SPHs are usually prepared. The use of a gas blowing technique [31] to produce foam during polymerization by adding a foaming agent such as sodium bicarbonate on an acid basis to produce bubbles [15]. Although both SAPs and SPHs are porous in structure, there is a difference between them as shown in Table (2).

Table 2. General features of superabsorbent polymers (SAPs) and super porous hydrogels (SPHs) [31].

	SAPs	**SPHs**
Commonly used monomers	Acrylamide, acrylic acid salts of acrylic acid including sodium and potassium acrylates	Acrylamide, acrylic acid, salts and esters of acrylic acid including sodium and sulfopropyl acrylates, 2-hydroxyethyl methacrylate
Method of synthesis	Bulk, solution, inverse suspension	Mostly aqueous solution
Initiating system	Thermal, redox	Mostly redox
Porous structure	Random closed to semiopen cells	Interconnected open cells
Final product	Particle	Any shape including particle, sheet, film, rod
Water absorption mechanisms	Diffusion (high), Capillary(low),	Diffusion (low), Capillary (high)
Free swelling capacity	Very high,	Very high
Retained water under pressure	High	Low
Applications	Where high swelling , fast medium rate of swelling is required	Where size - independent high and very fast swelling are required

Preparation of superabsorbent and super porous hydrogels described by the steps in Figure (14), the following application is performed regardless of the type of material used the monomer is first diluted with certain amount of water to reach a desired monomer concentration (Step 1). Dilution with water also makes it easy to handle the monomers. For instance, the water-diluted glacial acrylic acid possesses superior handling properties as compared with acrylic acid because of its lower freezing temperature. Normally, the monomer is mixed with water at room temperature under gentle mixing. To produce ionic superabsorbent, monomers, such as acrylic acid, may be neutralized to some degree, normally to 75 mol% (Step 2), followed by addition of a cross-linker (Step 3). Since neutralization can be accompanied by the sudden release of significant amounts of heat, a double-surfaced reactor equipped with external or internal cooling jackets or coils may be employed. All modern superabsorbent polymers are produced to possess large amounts of pores necessary to acquire fast water absorption property. This property can normally be achieved by generating gas bubbles. To produce foam during polymerization, foaming aid such as glacial acetic acid is added to the monomer solution (Step 4). For promoted polymerization, thermal and redox initiators, such as ammonium per sulphate or potassium per sulphate, are normally used. Oxidant and reluctant are added to the monomer solution under gentle mixing (Steps 5–6). Gas bubbles are generated by addition of acid-dependent foaming agent, such as sodium bicarbonate) Step 7) [15].

Super porous hydrogels are produced via adding of a foam stabilizer during the process (Step 4). Since the foam stability is essential for producing homogeneous SPHs, surfactants, such as PEO–PPO–PEO triblock copolymers, are used during the preparation process. The aqueous surfactant solution is added to the monomer solution and mixed under gentle mixing. Another unique step produce SPHs is using redox couple initiators such as ammonium per sulphate/sodium met bisulphite or potassium per sulphate/sodium met bisulphite (Steps 5–6). Almost all SPHs are produced using an oxidant/reluctant couple, while SAPs are produced via both thermal and redox systems [15].

The reactions involved in the preparation of SAPs and SPHs are cross-linking polymerization (which is also known as gelation) and foaming. Dispersion and dissolution of the bicarbonate (Step 7) increases the pH of the reaction medium to a level at which the initiator decomposes faster. As the formation of initiator radicals reaches a certain level, the polymerization reaction proceeds rapidly and the reacting mixture becomes viscous. Concurrently, bicarbonate interacts with the acid component of the system to produce CO2

gases required for the blowing process. The two processes, i.e., gelation and foaming processes need to be conducted in such a way to enable harmonized foaming and gelation. Since no foam stabilizer is normally used in the preparation of SAPs, the foam spontaneously collapses under its weight and shrinks into a smaller volume. Therefore, pore structures are not preserved in a controlled manner. Consistency of the hydrogel after its formation can affect the foam stabilization. For instance, polymerization of highly concentrated monomer solutions results in sudden gelation of the reacting mixture to a brittle and solid product. Thus, mobility of the polymer chains is prevented, and hence, the pores could be preserved to some extent. The foamed product is then dried and mechanically ground [15].

In case of SPHs, Super-porous hydrogels are dried under various conditions. First method, the bulky hydrogels are dried for a day at (60 ± 1 °C) in a food dehydrator. In the second method, bulky hydrogels are dried first by placing them in a small volume of absolute ethanol for each gel. After this initial drying step, the ultra-porous hydrogels are dried by placing them in absolute ethanol several times to ensure that all the water is replaced with ethanol. During the drying process, the soft and supple drogues that are super porous become hard and brittle. After drying was completed, the excess ethanol in the dried ultra-pore hydrogels was removed by draining with a paper towel, and then the ultra-porous hydrogels were dried in an oven at 55 °C for 1 day [32].

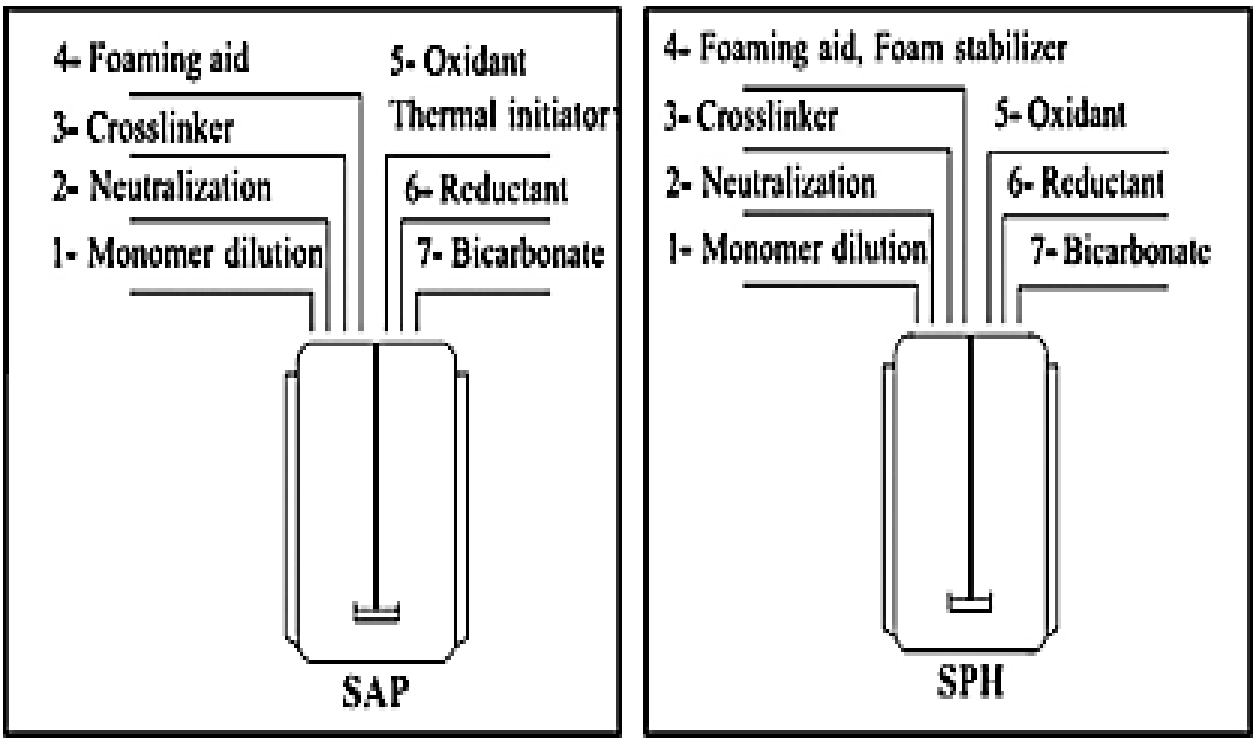


Figure14: Preparative steps in the production of SAPs and SPHs [15].

II-3-Methods of Physicochemical Characterization:

In order to design hydrogels with required performance and structure, identification and characterization of hydrogel network information is of great importance. Common techniques discussed below were selected to look at the structure and structure of hydrogels [27].

One of the most important studies and tools is the physico-chemical characterization of hydrogels such as the study of hydrogel swelling, infrared spectroscopy, X-ray diffraction analysis, electron microscopy, and optical microscopy. It is explained in detail below:

II-3-1-Swelling Study:

There are three ways to study hydrogel swelling:

a-Method:

The method of Japanese Industrial Standard K 8150 is used for the hydrogel, and the dry hydrogel is immersed in deionized water for 48 hours at room temperature on a cylindrical mixer. After swelling, the hydrogel is filtered through a 30-mesh stainless steel mesh and the swelling is calculated as follows [33]:

$$\text{Swelling} = \frac{W_s - W_d}{W_d} \qquad (1)$$

W_s: weight of hydrogel in bulge state.

W_d: weight of hydrogel in dry state.

b-Method:

Measurement of hydrogel swelling. In a volumetric flask (universal), the dry hydrogel (0.1-0.5 g) is dispersed in sufficient volume of water (25-30 ml) for 48 hours at room temperature, then centrifuged to obtain a mixture of layers of materials bound with water and non-absorbed water, then the free water is removed, and swelling can be measured according to method (1)[17].

c-Method:

Hydrogel swelling measurement according to Japanese Industry Standard K723 (JIS) . The dry gel was immersed in deionized water for 16 h and kept at room temperature. After swelling, the hydrogel is filtered using 100 stainless steel mesh. Swelling is calculated as follows [34].

$$\text{Swelling(times)} = \frac{C}{B} \times 100 \qquad (2)$$

where B and C are the weight of the hydrogel obtained dry and swelled, respectively.

II-3-2-Electron Microscopy (EM):

Electron microscopy (EM) is a technique for obtaining high-resolution images of biological and non-biological samples. High-resolution electromagnetic images result from the use of electrons (which have very short wavelengths) as a source of radiation illumination [35]. Scanning electron microscopy is useful in providing information about surface topography, morphology and polymer composition. The magnification in the SEM can be controlled up to a range of 6 orders of magnitude about 10 to 500,000 times. Figure (15) shows a photograph of the scanning electron microscopy instrument, which is a powerful tool widely used to capture the characteristic of the 'network' structure in hydrogels. Moreover, it has been shown that SEM can be applied to study network morphology [17].

Figure15: Image Electron Microscopy(EM) [17].

II-3-3-Infrared Spectroscopy:

FTIR (Fourier Transform Infrared Spectroscopy) is a useful technique for determining the chemical composition of a substance [36]. It is used to measure vibrational energy transitions, and to give information about the different types of chemical bonds, and the local chemical environment present within materials [17]. It is based on the principle that the basic components of a substance, i.e. chemical bonds, are usually excited and absorb infrared light at frequencies typical of chemical bond types. The resulting infrared absorption spectrum represents the footprint of the measured sample. This technique is widely used to investigate the structural arrangement in hydrogels [36]. Figure (16) shows the FTIR device:

Figure16: Image Infrared Spectroscopy [37].

II-3-4- X-Ray Diffraction Analysis:

X-Ray Diffraction, frequently abbreviated as XRD, is a non-destructive test method used to analyse the structure of crystalline materials by way of the study of the crystal structure, is used to identify the crystalline phases present in a material and thereby reveal chemical composition information [38], in Figure (17). photographic image of the X-ray diffraction analysis (XRD) instrument is given which can identify and characterize different samples including semi crystalline polymers. As soon as the sample is being irradiated with a beam of monochromatic X-rays, a part of light gets diffracted. These diffracted rays were analyzed based on angles of diffraction, and the intensity of the diffracted rays to give information about the structural makeup, % crystallinity and crystallite dimension, interplanar atomic spacing (d-spacing), orientation, and strains present in the polymer/polymer blend matrix can be determined by the XRD technique [17].

Figure17 : Image X-ray diffraction analyser [17].

II-3-5-Light Microscope:

An optical microscope is a tool for photographing the minute details of an object. It does this by creating an enlarged image through the use of a series of glass lenses. It focuses light on the sample, causing it to be magnified and extending the magnification range from 10 to 1000 times. The microscope has a wide range of contrast techniques. It provides information on the physical, chemical and biological properties of the samples and can be directly observed by the eye and recorded by photographic, video or computer techniques. Optical microscopes can be adapted to examine samples of any size, complete, segmented, wet or dry, hot or cold...etc. As the following Figure (18) shows [39].

Figure18: Image light microscope [40].

II-4-Hydrogel Application Methods:

There are two methods for applying Hydrogels, as soil conditioners to stabilize the surface of soils to inhibit crust formation and improve water- holding capacity or to improve the poor structure at greater depths by aggregation and to enhance plant growth [19].

II-4-1-Dry Method to Subsoil:

Dry polymer such as PAAm or PVA is applied to the subsoil by mixing with the sandy soil into depths of about 15-25 cm and then subjecting to wetting for swelling prior to cultivation. After the polymer has swollen the soil structure is improved and the water penetration and retention capacity increases, decreasing water runoff and erosion. This method is applied for long-term intentions as the polymer must absorb water prior to becoming beneficial, it is not recommended for immediate sowing [19].

II-4-2-Wet Method to Topsoil:

The polymer solution is sprayed onto initially wetted topsoil, followed by drying to create a water-stable aggregates that resist erosion. This method is particularly well adapted to sowing immediately afterwards and can also be adopted to reduce water consumption in irrigation systems where water losses occur due to the soil's poor ability to retain moisture. These wet polymer methods can also decrease soil erosion by being applied to topsoil or to driveways of irrigation. Surfactants have positive effects on aggregate stability, hydraulic conductivity and the distribution of conditioners [19].

II-Conclusion:

The study indicates the diversity of methods of preparing hydrogels that have passed through generations and were the focus of the attention of senior researchers, and this diversity knew a difference in the methods of preparation through the principle of preparation, starting with the monomer from which it was made. There is a difference in polymerization methods to form super absorbent and porous polymers for agricultural use. There are chemical and physical methods for manufacturing hydrogel, and studies are still ongoing and ongoing to develop methods for preparing hydrogels, to reach an easier method of preparation, low cost, better production, and diversity in the fields of use. The study also included the most important methods of hydrogel analysis to know the structure and surface structure of hydrogels. This study aims to know the results after manufacturing to verify the percentage of gels absorption of liquids and swelling, the ability to resist heat, as well as the chemical composition of the gels.

Through the multiplicity of methods for preparing hydrogels, we will discuss one of the methods of preparing hydrogel by blowing gas or foaming technique, and conducting a study on the gel to know its properties.

Chapter 03:

Experimental Work: Preparation of Hydrogel from Acrylic Acid

III-Introduction:

The composition of super porous hydrogels is similar to that of ordinary hydrogels, but the only difference is the addition of a foaming agent to prepare the super porous gels (SPHs) [41]. It is a chemically cross-linked hydrophilic polymer network that is able to absorb a large amount of water in a short time because it has a large number of pores compared to other gels [42]. The pores are interconnected if the processes of polymerization and foam formation do not coincide, and an important step in this process is the use of acid to control the polymerization process, and the addition of $NaHCO_3$ leads to the formation of foam and an increase in pH. It also accelerates the polymerization process and becomes within minutes [41], and is widely used in many fields such as health products and agricultural materials to improve the process of water consumption.

The study in this chapter deals with the production process of ultra-porous acrylic acid gels in our university laboratory. The use of a gas blowing (or foaming) technique by adding sodium bicarbonate to a mixture to produce carbon dioxide when reacting with acid to form pores in a hydrogel. The polymerization process is carried out as shown in Figure (19). The study also dealt with the swelling ability of the manufactured gel and its comparison with the commercial potassium poly acrylic hydrogel, as well as the study of the morphology of the gel by optical microscopy to detect the size of the pores.

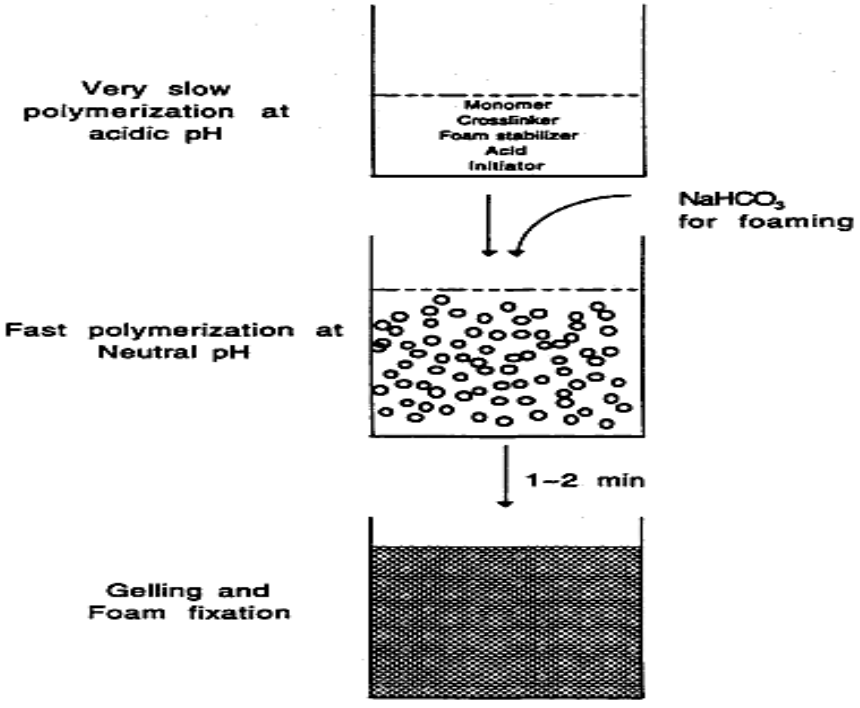


Figure 19: Schematic representation of the super porous hydrogel preparation [32].

III-1-The Purpose of the Experimental Work:

The synthesis of ultra-porous poly acrylic acid hydrogel with chemical formula as in Figure (20) was carried out by polymerization using gas blowing technique, and EDTA was used as crosslinking agent.

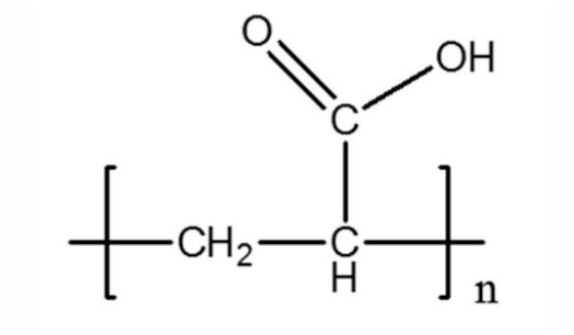


Figure 20: chemical structure of poly acrylic acid.

III-2-Materials and Tools Used:

Materials: We use high concentrations of materials

-Monomer: Acrylic acid AA (99% purity).

-Cross-linker: Ethylene diamine tetra-acetic acid EDTA (94% purity).

-Foam stabilizer: Gelatin Sweets.

-Initiator: Ammonium thiosulfate (96% purity)

-Initiation Catalyst: Ethylenediamie (99% purity)

-Foaming Agent: Sodium bicarbonate (99% purity).

In addition to Distilled water, NaOH (97% purity)

Tools Used:

- 3 Becher 100ml, Ring Stand, utility clamp, Burette, Graduated cylinder, Wash bottle, Spatula, Watch glass, Balances, pH meter, dryer.

III -3-Synthesis Method:

In this study, SPH hydrogel was synthesized by gas blowing technique using AA acrylic acid monomer and prepared in 100 mL Becher. The solution was stirred and mixed after adding each component.

Initially, 10 ml of 99% pure concentrated AA is prepared. Its acidity is diluted with a basic solution of sodium hydroxide. The latter is prepared by dissolving a mass of 1 g of solid sodium hydroxide in a volume of 5 ml of distilled water to obtain a solution with a concentration of 5 M. The low pH monomer solution (pH = 3) is titrated with NaOH as shown in Figure (21), This is for the purpose of reaching pH = 5.5, in order to reduce polymerization.

Figure 21: Titration of acrylic acid with sodium hydroxide to modify pH.

- After titration, 10 ml of monomer is taken in a 100 ml becher of monomer.

- After that, 500 mg of EDTA polymerization linker was added to the monomer, then the mixture was mixed for two minutes with a spoon, at the same room temperature.

- Then 500 mg of ammonium thiosulfate was added to the mixture, then mixed for two minutes This is the Initiator for polymerization.

- Then add 5 ml of the Initiation Catalyst Ethylene-diamine to the mixture and stir the mixture for one minute.

- Then a volume of 4.5 - 5 ml of distilled water is added with stirring, and this is for the purpose of diluting the mixture.

-Then 450 mg of gelatin foam stabilizer is added to the mixture and then the mixture is mixed for a minute with a spoon.

-Then add 1 g of sodium bicarbonate as a foaming agent to the mixture and then mix with a spoon for a minute in order to distribute bubbles, as it works to raise the pH value and speed up the polymerization process.

- Then 2.5-3 ml of acrylic acid is gradually added to the mixture and we monitor the amount of foam produced.

- Finally, we get a wet gel. As in the following Figure (22).

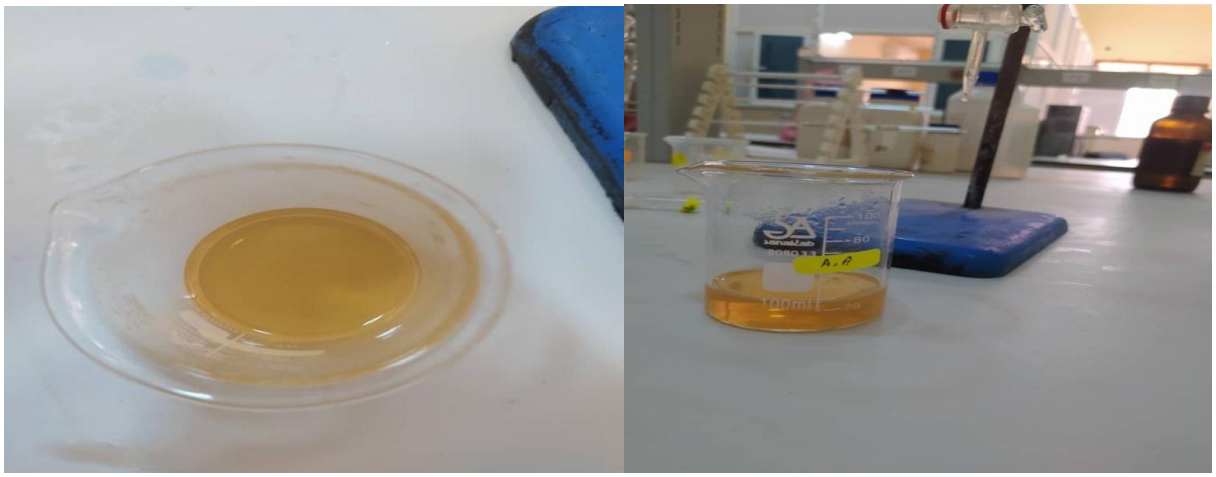


Figure22: Images wet gel before drying.

- This hydrogel is dried using the first method that we touched on in a previous chapter. Drying takes place in a food dehydrator at a temperature of 60 degrees for a whole day.

- Thus, we obtained a dry solid SPH hydrogel. As in the following Figure (23), then weighed and we got 8.5 g.

Figure23: Images wet gel after drying.

III-4-Hydrogel Analysis:

III-4-1-Microscopy Analysis:

The structure of the external porous surface of the SPH hydrogel as shown in figure (24) was examined using an optical microscope (OPTIKA) with a resolution of 100 times magnification.

Figure24: Image Wet gel under a microscope with a resolution of 100 times magnification.

III-4-2-Density of Hydrogels:

The density of the dried ultra-porous hydrogels was determined from direct measurements of mass and dimensions. The density of the ultra-pore hydrogel was calculated by the following relationship.

$$\mathbf{d}= \frac{W_d}{V_d}$$

where W_d is the dry weight of the hydrogel (8.5g).

V_d : Dry hydrogel volume The volume of dry hydrogel was calculated by direct measurements by placing a mass of dry hydrogel in a gradient regular cylindrical shape and then we measure the diameter and height of the gel in the cylinder and then calculate the volume of the dry gel using the following relationship:

D: Cylinder diameter.

H: The height of the hydrogel in the cylinder.

$$\mathrm{V} = \frac{\pi}{4} \times (D)^2 \times H \qquad V = \frac{\pi}{4} \times (5)^2 \times 0.5 = 9.81 cm^3$$

d= $\frac{8.5}{9.81}$ = 0.87

III-4-3-Swelling Study:

To determine the percentage of swelling (SPH), equation (1) was used

$$Q = \frac{(W_s - W_d)}{W_d}$$

-W_d Weigh a piece of dry hydrogel (8.5g).

-W_s Weigh the hydrogel piece in the swollen state after immersing it in an extra quantity of distilled water for 24 hours at room temperature conditions, then remove the extra water on the bulge with paper towels, and thus we get a hydrogel in the swollen state how much in the Figure (25), then weigh the gel We get weight Ws = 9.6g

$$Q = \frac{(9.6-8.5)}{8.5} = 0.12 = 12\%$$

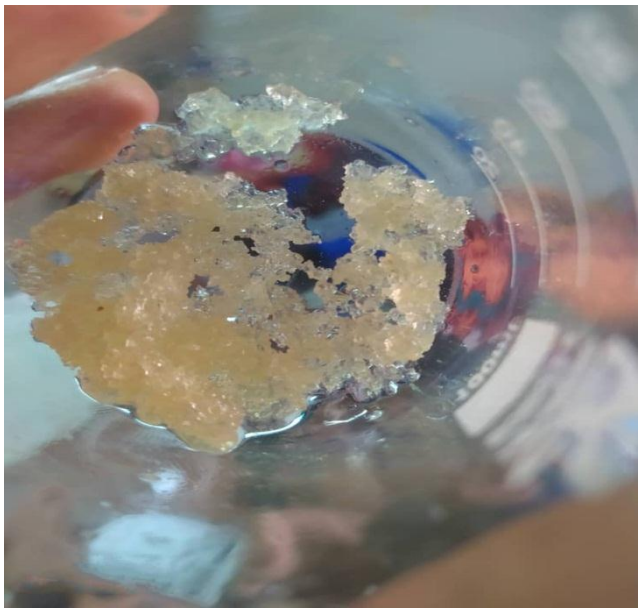


Figure25: Image Hydrogel in case of swelling.

III-7-Commercial Hydrogel:

Commercial Hydrogel (Polyacrylic Potassium) from ARTAGRO POLSKA produces innovative hydrogels for agricultural applications (Agro NANO Gel Basic), is a super absorbent cross-linked material (absorbs about 400-450ml/g), to improve the soil substructure, the hydrogel absorbs water and swells, creating crystals Effective in soil for 5 years and completely degrades after 10 years. As shown in the following Figure (26).

Figure26 : Images Commercial Hydrogel.

III-8-Hydrogel Analysis:

III-8-1-Swelling Test:

The swelling of the commercial super absorbent hydrogel was tested by taking a sample of M_d =1 g of it and placing it in 500 ml and then adding a volume of distilled water in increments of about 500 ml. We note that after an hour the water was absorbed and the excess water was dried with a tissue, then we weighed the sample after swelling, and we got a weight of M_s = 451 g , then the swelling was measured by the following relationship:

$$Q = \frac{(M_s - M_d)}{M_d}$$

$$Q = \frac{(451-1)}{1} = 450 = 45000\%$$

III-8-2-Rheological Evaluation:

Hydrogel viscosity was measured with the Master Smart L Rotary Viscometer from Fungi lab. The meter provides direct on-screen readings with great speed and accuracy of viscosity in cst /** and temperature as shown in Figure (27).

At the beginning of the viscosity range adjustment, choose a stainless steel rod (R2), set the rotational speed (100 rpm), and select the hydrogel density 0.8 g/cm3. A sample of saturated superabsorbent hydrogel with a volume of about 500 ml is prepared in Becher, then

we heat the latter to 60 ° C and then transfer it to the viscometer, which is measured for different periods of temperature from 60 ° C until it drops to 20 and constantly monitored.

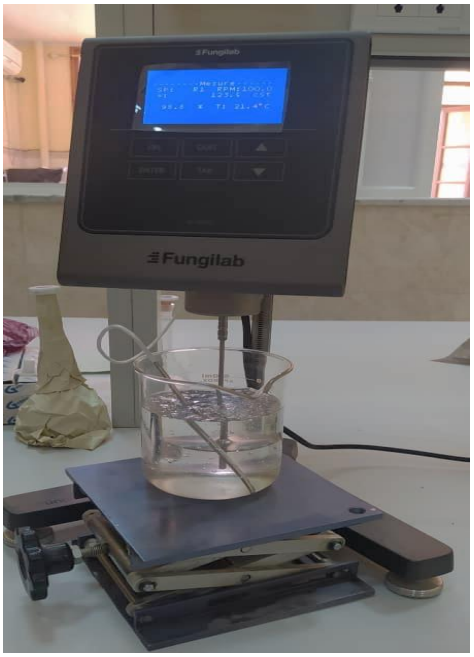


Figure27: Image Viscometer used in a study.

III-9-Results and Discussion:

III-9-1-Polymerization Process:

In this study, a super-porous hydrogel was prepared by gas blowing polymerization (or foam) resulting from the reaction of sodium bicarbonate with acid, in which excessive amounts of $NaHCO_3$ were used to control the foam volume with the amount of acid added, which was AA. To make it super porous, crystallization should start with the appearance of the foam after adding NaHco3, but little results were found in foam production and crystallization. This is due to the selection of monomer (type and concentration), cross-linker and initiator (type and concentration) and at low concentration the reaction cannot proceed completely due to the lack of free radicals provided by the primers. As well as foam stabilizer.

In our study there was no compatibility in the components (EDTA/ Ethylenediamie /Ammonium Thiosulfate). In the polymerization process due to the type and high concentration of the substances, as well as the gelatin in the fixing foam, rapid crystallization can be achieved by careful testing of the substances when preparing. Examples of how to make ultra-porous hydrogels of different monomers are shown in Table (3).

Table 03: Exemplary Formulas Used in The Synthesis of Super Porous Hydrogels [32].

Monomer Type	Monomer	Crosslinker	water	Foam Stabilizer	Acid	Initiator	Initiation	Foaming Agent $NaHCO_3$
AM	1000 µL (50% AM)	200 µL (2.5%)	460 µL	100 µL (10% PF127)	45 µL (AA)	40 µL (20% APS)	40 µL (20% TEMED)	90 mg
AMPS (Na salt)	1000 µL (30% AM)	40 µL (2.5%)		50 µL (10% PF127)	25 µL (AA)	20 µL (20% APS)	20 µL (20% TEMED)	90 mg
AA	500 µL	200 µL (2.5%)	500 µL	100 µL (10% PF127)		100 µL (10% V545)		15 mg
AA (Na salt)	1000 µL (PH~6)	200 µL (2.5%)	460 µL	100 µL (10% PF127)	25 µL (AA)	40 µL (20% APS)	40 µL (20% TEMED)	90 mg
ATMS	1000 µL (30% ATMS)	40 µL (2.5%)		50 µL (10% PF127)	30 µL (AA)	20 µL (20% APS)	20 µL (20% TEMED)	90 mg
HEMA	700 µL	100 µL (2.5%)		100 µL (10% PF127)		50 µL (20% APS)	50 µL (20% TEMED)	80 mg
HPMA	500 µL (in isopropanol)	200 µL (10% in DMSO)		90 µL (10% SL7605 in DMSO)		180 µL (10% APS)	90 µL (10% TEMED)	30 mg
SPAK	1000 µL (30% SPAK)	40 µL (2.5%)		50 µL (10% PF127)	30 µL (AA)	20 µL (20% APS)	20 µL (20% TEMED)	90 mg
VP	500 µL	200 µL (2.5%)	100 µL	50 µL (10% PF127)	20 µL (AA)	50 µL (10% V545)		20 mg
AM+SPAK	440 µL (50% AM) + 300 µL (50% SPAK)	250 µL (2.5%)		50 µL (10% PF127)	10 µL (AA)	30 µL (20% APS)	20 µL (20% TEMED)	100 mg
AM+AA	300 µL (50% AM) + 200 µL (50% AA)	100 µL (2.5%)	330 µL	30 µL (10% PF127)		20 µL (20% APS)	20 µL (20% TEMED)	120 mg
NIPAM+AM	1000 µL (20% NIPAM) + 200 µL (20% AM)	400 µL (2.5%)		100 µL (10% PF127) + 30 µL (10% SL7605 in DMSO)	50 µL (6N HCL)	50 µL (20% APS)	50 µL (20% TEMED)	60 mg

III-9-2-Drying Method:

The drying method used in our preparation. The use of a food dehydrator for a whole day at 60 degrees was not feasible in drying because there were remnants of raw materials deposited in the solution without interaction due to additional quantities when preparing. This makes it difficult to clearly detect the pores of the gel. A second method of drying can be used by washing the hydrogels with ethanol several times before drying to remove precipitated substances without interaction and then drying them in an oven for a day at 55 degrees, and the results are better in drying and studying its properties.

III-9-3-Swelling Capacity:

Super-porous hydrogels were manufactured from acrylic acid as described above, and an attempt to match the high swelling of commercial (potassium polyacrylic) gels. While it was possible to increase the ability to swell to some extent.

Swelling The most interesting property of hydrogels is their swelling. When it comes into contact with liquids, it begins to absorb the liquid, allowing it to increase in volume.

In our study, the swelling behavior of the composite PAA hydrogels was compared with that of the commercial hydrogels. The results showed that the latter had a high level of swelling and swelled well over time due to a large amount of water that was absorbed and reached the equilibrium value after a short period, the swelling percentage is high 45000% compared to the synthetic generation. The bloating rate is very low 12% after a long period of 24 hours. The amount of absorption and swelling was not great and was little or almost non-existent.

According to the percentage of hydrogel swelling, the porosity type can be categorized into 4 different types, such as porous hydrogels, micro porous, macro porous, and super porous. By the results obtained after swelling of the manufactured hydrogels, this gel can be classified as a non-porous hydrogel. Refer to the fact that these gels contain tightly packed polymer chains that limit the diffusion of the solvent across the free hydrogel matrix [43]. As shown in the figure by the light microscope in Figure (24), and this makes the inability to absorb water and increase its volume. It also cannot be useful and suitable for intended applications.

III-9-4-Hydrogel Porosity Study:

The structure of the ultra-porous hydrogels was examined under a light microscope as shown in Figure (24). after drying in a food dehydrator for a whole day at 60° and magnified by 100 times. It showed that the enlargement was not enough for the pores to appear clearly, which made that no pores appeared. Possibly the reason may be that the hydrogel pore size is small, which led to the small magnification accuracy used in our study, not being able to reach any pore significantly. Or it could also be that after adding a foaming agent the foam production and polymerization process did not take place completely, and some solvents and foam stabilizer remained in the hydrogel precipitated and this led to the inability to completely dry the hydrogel or the possibility that the drying condition used in our study somehow disrupted the channels Capillary and polymer chains and pores break down and this leads to gel shrinkage.

III-9-5-Study of The Effect of Heat On Viscosity:

Through our study to test the kinematic viscosity of hydrogel and its effect by heat using a rotary viscosity device by measuring torque, and with a change in temperature from (60 to 20℃), we noticed that the lower the temperature, the higher the viscosity values as shown in the graph (01).

We conclude through our observation of the obtained results that with a small change in temperature the kinetic viscosity of the hydrogel is affected and this reason is due to the cohesion forces between the hydrogel molecules, when the temperature decreases, the cohesion forces between the hydrogel molecules increase and vice versa. The increase in temperature also affected the degree of swelling and the composition of the gels after swelling, resulting in increased gonorrhea and a decrease in the amount of water absorption.

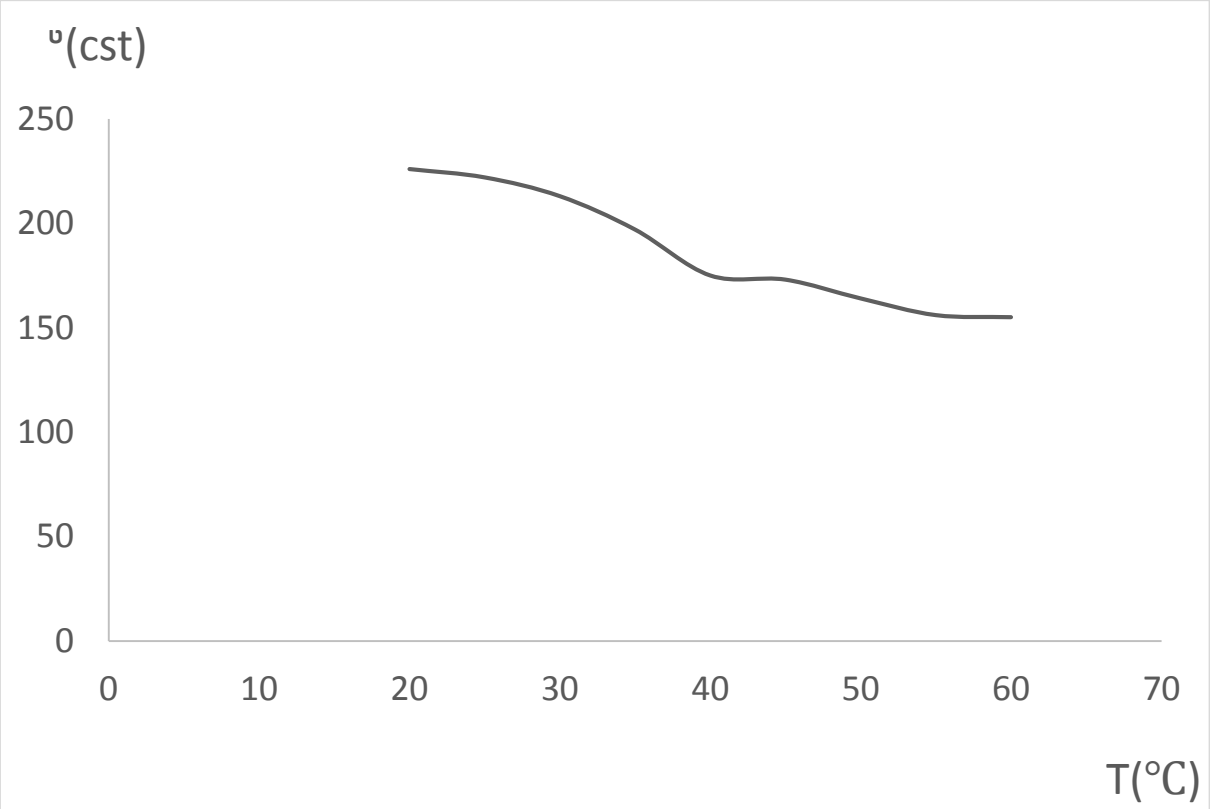


Figure28: Graph: Viscosity change by temperature change.

III-9-6-Effect of Initiator and Catalyst On the Polymerization Process:

Initiator concentration can affect the polymerization and properties of hydrogels, if the initiator concentration (Ethylene diamine / Ammonium thiosulfate) is excessive it reduces the polymer chain length and elasticity of the gels and with increasing gel turbidity, however if the initiator concentration is exceptionally high it will result in a polymer chain Too short and the polymers remain in solution form which can also affect the pH concentration of a solution .In turn, decreasing the amount of initiator increases the flexibility and length of the polymer chain but slows down polymerization, allowing oxygen to enter the solution and eventually producing a highly porous gel.

In general, for optimum polymerization, the concentration of the catalyst must be appropriate and sufficient to achieve the production of a porous gel [43].

III-9-7-Factors affecting swelling*:*

The swelling behavior of the hydrogel depends mainly on the hydrogel structure, polymerization process, the concentration of the cross-linking agent, and the size of the hydrogel particles [44].

-The effect of the cross-linking factor:

The concentration of the cross-linking agent in the hydrogel network is important because it directly affects the degree of swelling and thus the viscosity properties of the hydrogel [45]. With the increase of the cross-linked content in the hydrogel, the swell rate decreases significantly. This can be explained by the fact that the greater number of interrupted cross-links in the hydrogel leads to a restriction of movement in the chain of large molecules that does not allow water to penetrate and leads to a decrease in the swell rate [46]. If the concentration of the cross-linking agent increases, the condensation of the hydrogel and the structure of the hydrogels becomes more crowded due to the increase in the number of cross-links on the polymer chain, this density prevents the expansion of the structure on water absorption. There must be flexibility in the hydrogel structure so that it can expand and exhibit swelling behavior when a certain amount of water is absorbed [44].

-Hydrogel particle size effect:

Particle size is a major factor that has a direct effect on water absorption and retention. When the hydrogel particles decrease in size, the water absorption and retention properties are greater because the smaller size increases the surface area. It can absorb water within the three-dimensional structure of the hydrogel and the interstitial spaces created by the enlarged hydrogel particle, the smaller particle size and interstitial spaces increase with the greater the water absorption and water retention properties [44].

III-Conclusion:

This review noted the synthesis of polymers that swells automatically on contact with water and an innovative environmentally friendly class called SPH and compared them to the performance of commercial SAP superabsorbent polymers, which are new materials that swell quickly to a large volume regardless of their original size, and these materials tend to absorb a lot of water or liquids in a relatively short period.

Based on the result obtained, it can be concluded that the gels, which were made using polyacrylic acid gas technology, did not show any improvement in the water absorption property after testing the swelling capacity and confirming the absorption and after assessing the pore formation by light microscopy, and comparing it with the performance of potassium hydrogel common commercial applications for agricultural applications, they swelled more well than the hydrogels synthesized in this study. Poor performance due to deterioration in the condition and composition of polyacrylic acid as well as in the drying method. In order to improve the performance of this gel material, it is necessary to develop a good and suitable production process, installation and testing of materials.

Prospects:

The class of superabsorbent hydrogels will be of great interest to researchers in the era of nanofabrication. There is a need for miniaturization of hydrogels with increased durability, mechanical properties, and biocompatibility for new applications and versatility in fields of use. Variable methods of manufacturing are seen by replacing synthetic polymers with hydrogels from natural polymers. Due to its purity, high absorbency and environmental friendliness, it will be the main target for the coming decades, to achieve absorption requirements and reduce complexity.

General Conclusion

This review clarified the generalities of hydrogels composed of three-dimensional networks, composed of polymers of a special nature that are hydrolysable, as well as the field of use of hydrogels over the years, with multiple applications in agricultural, medical, and industrial aspects, and from the great diversity of hydrogels described The study described the classification of hydrogels on the basis of different chemical and physical properties, the source of the monomer from which it is composed, the method of its preparation, and its response to external factors, as well as biodegradation after time, the inclusion of a variety of materials based on hydrogel synthesis develops differences with varying degrees of Functional characteristics.

The method for preparation and design of hydrogels the process influences the production of hydrogels by various physical and chemical techniques. The study described an innovative class of environmentally friendly gels called SAPs and SPHs that rapidly swell to a large size regardless of their original size. This class is receiving serious attention from researchers in this era. Synthesized in several different ways, this class enhances durability and biocompatibility for new applications to reduce the complexity of hydrogel formulations, a primary goal for the coming decades.

In the experimental work, the study demonstrated the synthesis of a super absorbent and porous compound in an aqueous solution by polymerization, this technique is called gas blowing or foaming, and it was prepared through concentrated acrylic acid with an amount of EDTA binding agent to crosslink between AA monomers and Ethelendiamine as an initiator of the polymerization process, As well as adding the sodium bicarbonate foaming agent is important in this technique, which is the formation of foam in the solution through the appearance of gas bubbles and gas release, and this raises the pH value and accelerates the polymerization.

The production technology also included a number of factors affecting the design process, the polymerization led to a decrease in the quality and quantity of the product due to the high concentration of the reactants, which led to a slowdown and decrease in the polymerization process, as well as non-reactive substances remaining deposited in the gel that disrupted the drying process in these the study is due to the presence of fully unreacted substances during synthesis. These factors affected the polymerization as well as the swell capacity test and the study of surface porosity, the amount of water absorption, as well as the speed of reaching the swell equilibrium compared to the adsorption capacity test of

commercial highly absorbent potassium polyacrylic gel hydrogel. We conclude that the important factor that controls the quality of the hydrogel is the appropriate selection of the reaction materials and the design technique.

Recently, many networks based on hydrogels have been designed to meet the needs of different applications, and hydrogel synthesis continues to evolve over future generations to improve the performance of gels and the diversity of applications.

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