

## APPLICATION OF SUPERABSORBENT POLYMERS IN THE AGRICULTURE AND THE IMPORTANCE OF THEIR BIODEGRADABILITY - A REVIEW

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### Abstract

*This article aims to bring to light a relatively new strategy to ameliorate some problems that the agricultural sector faces in the current situation at a global level, such as water scarcity, drought, continuous degenerative processes of the soil or even the diseases caused by plant pests. One of the novel solutions that can be applied to balance the current situation is represented by the using of biodegradable superabsorbent polymers, due to their capacity, representing a reservoir able to store water, nutrients, or pesticides and then release them a constant flow, ensuring an optimal and beneficial ratio at the soil and plant level. They have numerous beneficial properties and advantages, being found in a multitude of fields, one of the most critical properties being represented by their biodegradability. Currently, the most "green" methods are being sought for obtaining these superabsorbents polymers to be used on a large scale and presenting a ratio of biodegradation as high as possible and no ecotoxicity after their application.*

**Key words:** superabsorbent, biopolymer, biodegradability, hydrogel, water storage.

### INTRODUCTION

In the current situation, the global population faces severe water shortages throughout the year with areas where water resources are limited for at least one month in a year (Kathi et al., 2021). Agriculture is the sector that uses over 70% of fresh water, therefore, according to Abobatta (2018), in order to feed a population of approximately 9 billion individuals, until the year 2050, a calculable 50% increase in the agricultural production would be required and also 15% of water withdrawals.

Millions of hectares of land are becoming unproductive every year due to the agricultural activities becoming less and less sustainable which results in the triggering of soil degenerative processes (Turioni et al., 2021).

The sandy, calcareous, alkaline and acidic soil are in which restoration is necessary, they have very low productivity and are poor in terms of their biological or physico-chemical properties (Rajakumar & Sankar, 2016).

Drought is one of the most harmful, expensive, and complicated natural disasters that has an

impact on many facets of civilization (Craft et al., 2015). Low soil moisture and high temperatures prevent plants from growing properly, which reduces agricultural yield and quality (Skrzypczak et al., 2020). Water stress, particularly during the crucial development phase of the farmed crop, is one of the most significant elements impacting plant growth and agricultural output (Barajas-Ledesma et al., 2022). The most popular irrigation technique involves directly watering the crop surface; however, this doesn't address the drought issue (Skrzypczak et al., 2020). The introduction of contemporary micro-irrigation technologies, such as low-pressure micro-sprinklers and drip irrigation systems, can now alleviate the problem by substantially lowering irrigation water consumption and boosting water usage efficiency (Abd El-Wahed & Ali, 2013; Deshmukh & Hardaha, 2014). Yet, these high-tech procedures are specifically utilized in high-value crops and need substantial capital expenditures, ongoing running expenses, and farmer experience (Patra et al., 2022). The use of hydrogels with strong water absorption and

retention capabilities, even at high temperatures, is one of the temporary solutions to these deficiencies (Skrzypczak et al., 2020). The hydrogel functions as a reservoir, storing and releasing a steady flow of water and nutrients required by plants to thrive (Kurrey et al., 2018). According to the Food and Agriculture Organization of the United Nations (FAO), plant diseases can lead over \$220 billion in global economic losses annually, while plant pests contribute to losses of 20-40% of overall crop yield globally (Pirzada et al., 2020). Pesticide delivery methods based on hydrogels have indeed attracted attention, and various patents have been obtained based upon those particular agricultural purposes (Montesano et al., 2015). The majority of traditional hydrogels on the market are acrylate-based products which aren't biodegradable and are considered potential soil pollutants. However, with the increased focus on environmental protection issues, biodegradable hydrogels are attracting a grown interest for considerable commercial uses in agriculture (Cannazza et al., 2014).

Although most superabsorbents are composed of synthetic polymers (often acrylic monomers) because to their favorable cost-performance ratio, for environmental considerations, the notion of partially or entirely substituting those synthetic materials with sustainable and "green" alternatives should be studied (Michalik & Wandzik, 2020). The ecologically responsible manufacture of biodegradable hydrogels from natural resources is in high demand (Monadal et al., 2022). Among the most important polysaccharides integrated into hydrogels with potential for large-scale agricultural applications are chitosan (Nangia et al., 2018), alginates (Thakur et al., 2018), starch (Ismail et al., 2013), and cellulose (Demetri et al., 2013; Tomadoni et al., 2019).

Numerous natural ingredients have recently been effectively incorporated into hydrogels to increase their biocompatibility and biodegradability, resulting in new biodegradable superabsorbent hydrogels with importance in the agricultural sector, based on starch, natural and semi-synthetic chitosan, cellulose, pectin,

gum arabic and cashew gum (Čechmánková et al., 2021).

## MECHANISM OF ACTION

Hydrogels, furthermore known as "root watering crystals," "water retention granules," or "raindrops" (Patra et al., 2022), are cross-linked polymers with hydrophilic groups that can absorb a significant quantity of water without being dissolved in it, retaining both water and nutrients and then releasing them over time (Mahinroosta et al., 2018). Because of their cross-linked structure, hydrogels retain the equilibrium of their networks when inflated, enabling them to remain stable in a range of settings. Certain hydrogels may even absorb aqueous fluids up to hundreds of times their weight and are hence referred to as super absorbents (Mignon et al., 2019). Hydrogels are unusual materials due to their softness, intelligence, and the capacity to retain water (Choudhary et al., 2014).

An ideal agriculturally effective hydrogel should meet several characteristics, including "substantial absorption ability, adjustable absorption rate, high absorption when exposed to water, high gel fraction after crosslinking, low cost, high stability after swelling and during storage, non-toxicity, and rewetting capacity" (Michalik & Wandzik, 2020).

The hydrogel is composed of a system of parallel polymer chains which are commonly joined together by cross-linking agents (Narjary et al., 2013).

The cationic hydrogels adhere to clay components and behave as flocculants, whereas anionic hydrogels can form bonds with clay as well as other negatively charged particles via ionic bridges (calcium and magnesium). The superabsorbent's capacity to absorb water, form aggregates and preserve soil structure is directly influenced by the attraction between the polymer and the solutes and soil particles in the environment, as a result, "the more cross-linked the polymer, the tighter the network" (Rajakumar & Sankar, 2016).

## CLASSIFICATION

Hydrogels can be classed based on a variety of factors, but the primary criterion for classification is their origin. The two basic varieties are synthetic and natural. Natural hydrogels (collagen, agarose, gelatine) are composed of polysaccharides with the capacity to form a hydrophilic chemical structure with high biocompatibility, whereas synthetic hydrogels (hydrophilic polymers) are created by chemical stabilization of hydrophilic polymeric materials in a three-dimensional network (Skrzypczak et al., 2020).

Hidrogels can be classified using the criteria listed in Table 1.

Table 1. Classification of hydrogels

Criterion of classification	Type of hydrogel	Reference
Origin	- syntetic - natural	Skrzypczak et al., 2020
Physical-chemical properties	- physically stable - chemically stable	Elshafie & Camele, 2021
Method of preparation	- homopolymer - copolymer - semi-interpenetrating networks - interpenetrating networks	Laxmi et al., 2019
Configuration	- amorphous (non-crystalline) - semicrystalline (complex mixture of amorphous and crystalline phases)	Garg & Garg, 2016
Physical appearance	- solid - semisolid - liquid	Varaprasad et al., 2017
Physical properties	- conventional - smart	Bustamante-Torres et al. 2021
Cross-linked chain charge	- nonionic - ionic - amphoteric - zwitter	Khan et al., 2016
Pore size	- non-porous - microporous - super porous	Devi & Gaba, 2019
Degradability	- biodegradable - non-biodegradable	Vinchhi et al. 2021
Response to stimuli	- thermosensitive - sensitive to magnetic and electric field - sensitive to the composition of solvents - sensitive to pH - sensitive to sound and molecular species	Ahmad et al. 2022

The majority of traditional hydrogels on the market are acrylate-based products; the type of crosslinking agent used in chemical polymerization methods strengthens the bonds between

the chains; as a result, as compared to their natural equivalents, the compounds are not biodegradable or degrade at a considerably lesser rate, and thus might be regarded a concern to possible soil contamination (Mallik et al., 2018). Given the increased concern about environmental problems, there is a high need for environmentally friendly biodegradable hydrogels that do not cause soil deterioration or phytotoxicity (Skrzypczak et al., 2020). Among natural hydrogels, the polysaccharide hydrogels are particularly of interest because they are biodegradable, have renewable capacity, present low-cost and nontoxicity, and simple to produce from easily accessible precursors (Turioni et al., 2021).

## ADVANTAGES AND DISADVANTAGES

The usage of hydrogels in agriculture can provide the following benefits: water conservation, resistance to biotic and abiotic drought stress, improved soil quality, decreased seedling mortality, reduced irrigation frequency and water consumption, and reduced use of fertilizers and pesticides (Guillherme et al., 2015). They prevent soil erosion caused by surface runoff as well as fertilizer/pesticide leakage into groundwater (Sarkar et al., 2017), and also increase soil physical properties by increasing water retention and infiltration capacity, reducing the necessity of continuous watering (Skrzypczak et al., 2020).

Hydrogels offer a wide range of uses, including agriculture, drought control, water saving, industrial planting and municipal gardening (Elshafie and Camele, 2021). Apart from agricultural sector, they have been used in the following areas: biosensor (Ahmed, 2015), antigen delivery systems (Ishii-Mizuno et al., 2017), tissue engineering and regenerative medicine (Wei et al., 2016), controlled drug release (Zhao et al., 2016), therapeutic applications (Schulze et al., 2016), antifouling paints (Wang & Wei, 2016), artificial snow (Ahmed, 2015), biomedical and pharmaceutical applications (Wang et al., 2015), dressing and sealing (Ebrahimi et al., 2015), drug delivery systems (Ye et al., 2016) and water purification (Tran et al., 2017).

Among the general drawbacks of the usage of hydrogels, the most common are the non-

adherent nature, the low mechanical strength, the nutrient/agrochemical loading weight, or the interference of dissolved salts (Rajakuar & Sankar, 2016).

The expensive cost of hydrogels is a deterrent that has severely limited their broad acceptance. (Choudhary et al., 2014).

One of the primary drawbacks of hydrogels is that the majority of them are polyacrylamides (recognized carcinogen that endangers both the environment and human health) generated from fossil fuels, which have limited environmental degradability, yielding acrylate and acrylamide groups in the soil (Barajas-Ledesman et al., 2022).

The water absorption capacity could be limited when salts are present in the solution, causing a deficiency in the balance between the system's osmotic pressure and the hydrogel's expansion rate (Neto et al., 2017).

According to Laxmi et al. (2019), the characteristics of an ideal hydrogel are: "colorless, odorless and non-toxic materials, with high water absorption capacity, very good functionality even at high temperatures, improve the physical condition of the soil (porosity, bulk density, water holding capacity, permeability), having desired absorption rate according to application requirements, cost-effective, high durability and stability in the swelling environment and during storage, pH-neutrality after swelling in water, photostability, ability to rewetting, high biodegradability without the formation of toxic species following degradation".

## PROCESS OF BIODEGRADATION

A biodegradable material has the property of being entirely utilised as a carbon and energy source enabling microbial growth (based on the OECD definition of "ultimate biodegradability"). The degradation process produces carbon dioxide, mineral salts, water, and new biomass under aerobic circumstances. Methane and/or low molecular weight acids may additionally be generated in anaerobic circumstances (Harrison et al., 2018).

Hydrogels are classed as either non-biodegradable or biodegradable (Vinchhi et al. 2021). Non-biodegradable hydrogels (majority of synthetic ones, obtained through chemical cross-linking) are distinguished by their resilience to

the impacts of environmental stimuli as well as their capacity to retain their chemical, physical, and structural qualities over time. The great majority of natural polymer hydrogels, on the other hand, may be categorized as biodegradable. When exposed to natural conditions, the three-dimensional structure is prone to deterioration due to enzymatic and bacterial action (Oladosu et al., 2022).

Biodegradability is a highly sought quality in hydrogels intended for agricultural use. Many studies have been undertaken to assess the biodegradability of various hydrogels. Acrylic acid or acrylamide have mostly been used to obtain synthetic polymers, which may represent environmental risks due to their low biodegradability (approximately 10% per year) (Prakash et al., 2021).

According to research, the hydrogel is susceptible to UV radiation and dissolves to form oligomers. Polyacrylate degrades at rates of 10-15% each year into water, carbon dioxide, and nitrogen compounds as it becomes increasingly vulnerable to aerobic and anaerobic microbial breakdown. The polymer's molecules become too large to be absorbed by plant tissue and therefore have no bioaccumulation capability (Rajakuar & Sankar, 2016, Neethu et al., 2018).

Mineralization can also occur as a result of biological degradation, such as that caused by fungi. The biological breakdown of several types of polymers in soil is quite successful, especially under circumstances that significantly enhance solubility. For instance, under aerobic circumstances similar to the breakdown of organic matter in forest regions, the biodegradation of acrylate-based hydrogels in municipal compost has been accomplished at a rate of 1 to 9% per year (Elshafie & Camele, 2021).

Variations in visual appearance, mass, or mechanical qualities take place during different phases of biodegradation, making it critical to determine the moments where such physical changes are best assessed and what appropriate information, they may offer regarding the polymer breakdown. Biodegradation is commonly separated into three stages: "biodeterioration, bio fragmentation, and microbial assimilation". The mechanical properties of the material are commonly

changed throughout the biodeterioration stage and the beginning of fragmentation stage. As biodegradation progresses, they are followed by modifications in visual appearance and mass loss, establishing a primal assessment of biodegradation (Harrison et al., 2018).

## **METHODS FOR ASSESING THE BIODEGRADABILITY OF HYDROGELS**

One of the most commonly assessment method of the biodegradability of hydrogels is the *soil burial method*.

The percentage of biodegradation and the duration of the process could differentiate based on the materials and the method used. Table 2 showcases the compared weight loss percentage of several hydrogels after biodegradation, based upon the materials utilised for the synthesis of the hydrogels and the number of degradation days. As it could be seen, using the soil burial method, most of the hydrogels have a percentage of biodegradation around 80-90% on a 70-80 days trial.

The highest percentage was obtained by Saruchi et al. (2015), 92.29% in 77 days trial on gum tragacanth-acrylic acid-based hydrogel while, Choudhary et al. (2022) obtained for their gellan gum, ammonium persulfate, acrylic acid, N, N'-methylene bisacrylamide based hydrogel, in a 22 days trial, a record of 86.71% biodegradation rate (Table 2).

Taghreed et al. (2022) buried in pots filled with garden soil, their synthesized hydrogels (1g) equidistantly (3 cm apart). The weight of each sample was determined by extracting the samples every 7 days, rinsing with water, and drying at 70°C. Visual evaluation, changes in morphology (SEM), chemical structure (FTIR), and weight loss (WL) analyses can attributed to measure the level of degradation at various phases of biodegradation:

The weight loss (WL) of the samples could be obtained using the following equation: “ $WL (\%) = \frac{W_i - W_f}{W_i} \times 100$ ” where  $W_i$  represents the initial weight of the samples before the biodegradation process, while  $W_f$  represents the weight of the samples after specified time intervals of biodegradation (Durpekova et al., 2021). The rate of deterioration, according to Choudhary et al. (2022), is highly reliant on various parameters that impact microbial

proliferation, such as pH, oxygen concentration, temperature, mineral nutrition supply, and moisture. The percentage weight loss rises with time, which might be caused by residual or low molecular weight macromers dissociating during the testing.

Kenawy et al. (2021) assessed biodegradability by monitoring the weight loss of soil samples over time. Dried gel samples were weighed (1 g) and then buried in soil (maintained at 20% moisture) at a depth of 15 cm for 150 days. The buried samples were examined at certain time intervals, washed with distilled water, dried under vacuum at  $60 \pm 2^\circ\text{C}$  for 24 h, and then conditioned in a desiccator for at least one day. A continuous weight loss of the sample was observed over time and after 160 days a total weight loss of about 60% was reached showing good degradability in soil.

Choudhary et al. (2020) obtained by microwave-assisted synthesis, a new biodegradable superabsorbent Agr/GE-co-MA/AA (agar-agar gelatin copolymerized methyl acrylate and acrylic acid hydrogel) developed as an effective water retention agent. They determined that the degradation of Agr/GE-co-MA/AA hydrogel in soil and sand is a direct result of the activity of microorganisms, having no harmful effects on the fertility of sand and soil and improving organic matter in the agricultural field.

Another common method of determining the biodegradability of hydrogels is through *composting*.

Composting is an aerobic technique that manages solid waste, in which biodegradable materials are biologically digested into humus (a valuable nutrition source for increasing soil fertility and agricultural production) in the presence of microorganisms under supervised conditions such as temperature, aeration and humidity (Pires et al., 2022).

Sharma et al. (2014) used the compost collected from the municipality sewerage plant in Solan, Himachal Pradesh, India. The hydrogel samples of almost equal weights were buried in pots in the compost at the depth of 10 cm. Each day the compost in the pots was fed with microbial concentrate collected from the sewerage plant site and the biodegradability of the hydrogels was measured for 60 days up to specific time interval. The samples were taken out, washed with distilled water and dried in vacuum oven at

60°C followed by the weighing process. After 60 days, the hydrogels tested deteriorated at a rate of 1.07 mg/day for the Gg-cl-poly(AA)

hydrogel and 90% at a rate of 1.5 mg/day for the Gg-cl-poly(AA-IPN-aniline) hydrogel.

Table 2. Comparison of the biodegradation of hydrogels using the soil burial method

Hydrogel	Materials	Percentage of Degradation	Total days	Reference
Gum tragacanth-acrylic acid based hydrogel	Gum tragacanth, Acrylic acid	92.29	77	Saruchi et al., 2015
L/KJ/SA hydrogel	Lignosulfonate, Sodium alginate, Konjaku flour	20	120	Song et al., 2020
Lipase catalyzed hydrogel-IPN of GT with poly(AAm) and poly(MAA)	Gum tragacanth, Acrylamide, Methacrylic acid	81.26	77	Saruchi et al., 2019
CS50 hydrogel	Cassava starch, Polyacrylamide	80	30	Junlapong et al., 2020
Xanthan gum based hydrogel (semi-IPN)	Xanthan gum, Polyacrylic acid	78.3	70	Sukriti et al., 2017
GG-cl-poly(AA)	Gellan gum, Ammonium persulfate, Acrylic acid, N, N'-methylene bisacrylamide	86.71	22	Choudhary et al., 2022
Av-cl-poly(AA)	Aloe vera powder, Acrylic acid, Glutaraldehyde, Ammonium persulfate	90	70	Saruchi et al., 2023
CAP hydrogel film	Chitosan, Acetic acid, Acrylonitrile, Polyol, Bisacrylamide	90	42	Kouser et al., 2018
Neem gum-grafted poly (acrylamide) hydrogel	Neem gum polysaccharide, Acrylamide	90	28	Malviya et al., 2019
PVA/Water Hyacinth (PW) hydrogel	Polyvinyl alcohol, Water-hyacinth	12.86	42	Hossain et al., 2021
Gum rosin and psyllium-based hydrogel	Gum rosin, Psyllium	86.8	63	Wadhwa et al., 2020
Enzymatically catalyzed IPN	Lipase as initiator, Glutaraldehyde, Acrylic acid, Acrylamide	86.03	77	Saruchi et al., 2016
CMC/P4VP hydrogel	Carboxymethyl cellulose, Poly (4-vinylpyridine), N, N- methylene bis-acrylamide	50	5	Mohamed et al., 2022

**Vermicomposting** is another used method to determine the biodegradability of hydrogels. Vermicompost is the end result of a biodegradation involving a wide range of worm species, most notably red worms, white worms, and various other earthworms and, according to the study by Choudhary et al. (2022) biodegradation by soil burial test resulted in lower degree of less weight loss than vermicomposting. This could occur based on the fact that the vermicompost contains more types

of microorganisms than regular garden soil, which accelerates the breakdown process. Because of its high NPK content, as well as its capacity to strengthen the structure of the soil and store more water, vermicompost has a higher breakdown rate.

In the study assessed by Bandyopadhyay et al. (2019), the hydrogel film showcased an 80% rate of degradability in 28 days using the vermicomposting method.

Saruchi et al. (2023) assessed the biodegradability of a newly synthesized Av-cl-poly (AA) hydrogel over a period of 70 days using all three of the methods. The percentage of biodegradation in the study has proven to be 90% soil burial method, 93% vermicomposting and 94% composting.

The study of biodegradability with the white fungus of the polyacrylate and polyacrylamide copolymer in the soil along with the soil microbiome was explored. It demonstrated that microbial degradation was significantly lower than degradation paired with fungus or bacteria. The deterioration, however, was adequate for certification. In an open environment degradation research, it was conclusively demonstrated that microbial activity was responsible for the deterioration of the polymer-based hydrogel (Prakash et al., 2021).

Turioni et al. (2021) investigated the degradation of hydrogels using home-made devices that allowed indirect interaction between hydrogels and soil. Deionized water enriched with chemicals/microorganisms from the soil layer was deposited in the top tube to assure hydration, the hydrogel was placed in a cell created between two Falcon tubes in contact with two synthetic fabric discs. A rubber band linked the two tubes together, which was kept in place by two more rubber bands. This configuration allowed the operator to open the system and enter the cell containing the hydrogels.

There are a variety of analytical techniques and methodologies that may be used to supplement physical testing methods for determining biodegradability, including scanning electron microscopy - SEM (Kolya & Kang, 2022) transmission electron microscopy - TEM (Shaghaleh et al., 2022), thermogravimetric analysis - TGA (Songara & Patel, 2021) and Fourier transform infrared spectroscopy - FT-IR (Bora & Karak, 2022).

## CONCLUSIONS

The purpose of sustainable agriculture is to improve output while inflicting as little environmental damage as possible. Hydrogels might be used to alleviate drought stress and increased soil degradation, both of which represent a serious danger to agriculture.

Although various studies regarding the application of hydrogels in agriculture showcase their tremendous value, the cost and potential toxicity from biodegradation constitute issues that must be addressed during the following decade by using hydrogels that use non-toxic materials, possess elevated capability to absorb water, excellent functionality even at high temperatures, and, most importantly, high biodegradability without the generation of harmful compounds.

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