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RESEARCH ARTICLE

Sustainable Irrigation through Application of Hydrogel: A Review

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ABSTRACT

Agricultural sustainability is essential to enhance food and water security, particularly in the context of climate change. In the recent past, applications of hydrogels in agriculture have received substantial attention among researchers as well as among farmers. This review elaborates on various aspects of hydrogels such as classifications, ideal properties for agricultural application, and interaction mechanisms with soil and plants. The experimental methods for determining hydrogel properties were given specific attention as properties such as swelling, retention, slow release, and degradation are of vital importance to agricultural sustainability. The studies conducted over the years on the effect of hydrogel application on different crops are reviewed. Several hydrogel studies demonstrate significant improvement in water consumption, water use efficiency, crop growth and yield parameters. The review looks into hydrogel degradation mechanisms in soil and also the 'test methods' for assessment of biodegradation. The gap areas in research on hydrogels and agricultural sustainability have also been identified. The need for developing a framework for the evaluation of the suitability of hydrogel for agricultural applications has been brought out. The review would encourage further research on enhancing the ideal properties of hydrogel and synthesizing with natural polymers. The use of hydrogel in agriculture for controlled nutrient release could be an alternative to conventional release methods for fertilizers and pesticides, thereby reducing the environmental footprint. The reduction in water footprint in major crops such as paddy and wheat through hydrogel might establish a shift towards sustainable irrigation practices if adopted on a large scale. Integrating innovative solutions with environmental-friendly hydrogels in the coming decades will contribute to the pursuit of achieving sustainable development goals.

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Introduction

Water is the most consumed resource on the planet. Scarcity of water is a threat to most nations, and is currently a pressing issue in most developing nations, owing to climate change, and the increasing trend of temperature anomalies (Allen et al. (2018)). Increase in human activities such as agricultural production, and rapid domestication of animals have had a profound impact on the resource balances in the ecosystem of the planet leading to uncertainties in

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climate shifts (Smith & Zeder (2013)). These changes are generally not expected to be distributed equally and will much be dependent on regional climatic variations, resource availability and adaptive capabilities. Moreover, those nations not having participated in the accumulation of greenhouse gases will experience the highest environmental harm from climate change (Lelieveld et al. (2012)).

Extreme temperature events and drought frequency have increased in the recent decades. Several studies have been done with respect to the impact of climate change on precipitation and irrigation. In India, it has been predicted that an increase in irrigation storage is essential to keep the agricultural production at level with the demand due to decline in groundwater reserves in semi-arid regions and shifts in surface water distribution across river-fed irrigation plains (Devineni et al. (2013)). It is claimed that the number of drought events over the past decade has worsened and the pattern of monsoon rainfall contributing to 80 % of Nepal's precipitation has become more erratic since 2000 (Jha et al. (2016)). Each year has been hotter than the previous year in the African continent for the past 20 years. It is estimated that by 2080, the average temperature across Africa would increase by 4.5 °C with drastic changes in precipitation patterns (Rosenstock et al. (2018)). In China, the predictions show that there will be a temperature increase of at least 1.5 °C by the year 2100, and the precipitation would be increasingly unpredictable and more erratic with increased frequency of droughts and floods in the coming years besides more possibilities for heatwaves (Piao et al. (2010)). Depletion and scarcity of water poses a major obstacle towards development. Agricultural sector is the largest consumer of water and would come to bear the greatest blow from water scarcity issues (Roy et al. (2019)).

The "sustainable development goals" (SDGs), and "climate-smart agriculture" (CSA) are guiding frameworks for establishing sustainability in terms of food security, water availability, and production and consumption (Rosenstock et al. (2018), ECOSOC (2019)). It is reasonable to reduce consumption while increasing crop production to overcome the issues of excess consumption and reduced yield. Soil moisture and soil nutrient content are major deciding factors to ensure high yield of crops. Intermittent absence of water for crops such as paddy can lead to heavy losses for the farmers as well the society. Continuous supply of water under ordinary conditions is a necessity for the cultivation of such crops. In semi- arid regions, the crops such as paddy and wheat cultivated are either rainfed or through canal irrigation (Devineni et al. (2013)). The availability of water for rainfed rivers is uncertain with changes in precipitation patterns due to climatic variations. It is important to look into alternatives which can contribute to a better crop production environment with the help of sustainable water use approach. The quantity of water consumed by crops mainly depends upon the irrigation methods, Agro-meteorological parameters such as evapotranspiration, and the soil properties (Jacoby et al. (2017)). The conventional method of irrigation - furrow irrigation, is shown to have a high rate of evapotranspiration, low grain yield, and high erosion and leaching of soil from cultivated land (Sarkar et al. (2012), Bhattacharya (2018)). Around 40% of the world's freshwater is consumed by conventional irrigation methods in the production of rice (Parthasarathi et al. (2018)).

To reduce water consumption, control over irrigation practices and soil conditions could be possible. Irrigation planning is usually done to ensure that the amount of water supplied to the plants maintains a balance between the available water for plants in the growth medium (soil, mostly) and the amount of water consumed by the plant for growth and transpiration. The factors that can be considered to maintain the balance are the soil-water potential and the available water in the soil (Agaba et al. (2011)). Prediction models for short and long-term water resource management in irrigation have been developed. Ines et al. (2006) combined remote sensing-simulation modeling and genetic algorithm optimization to explore water management options in irrigated agriculture.

Surface drip irrigation and subsurface drip irrigation have shown to reduce water consumption by at least 70% (Smith & Zeder (2013)). (Parthasarathi et al. (2018)) showed that an aerobic drip irrigation system for rice cultivation could give a 39% higher economic return with a 49% reduced water consumption. Although subsurface drip irrigation is a very efficient irrigation method, it has had relatively limited expansion due to several disadvantages such as the clogging of emitters, difficulty of detecting leakages and repairing them (Frantz et al. (2005)).

An alternative approach is the use of soil conditioners. They help in reduced soil erosion, water retention in soil, reduction of high infiltration rates, prevention of fertilizer and pesticide runoffs, and reduction of evaporation of water in irrigated lands. Recently, several studies have been done towards the use of soil conditioners in regions with water scarcity and low precipitation (Narjary et al. (2012)). Farming communities began to use manure (organic matter), straw mulch, bitumen (treated and untreated), bitumen emulsions as soil conditioners but as time progressed, they have started using polyacrylamide (PAAm), a hydrophilic polymer (Tayel & El-Hady (1981), De Boodt (1975)). PAAm was first reported to be used for highway embankment stabilizations using plant growth in France, where dry unfertile lands were turned to well established vegetations (De Boodt (1975)). Studies were done in 1976 using a gelating material under the name verdyol for soil conditioning. Tayel & El-Hady (1981) proposed a supergel - a hydrophilic polymer which forms gel immediately on contact with water, for soil conditioning in sandy soil. These studies showed that hydrophilic polymers with swelling properties had the capacity to be built into soil conditioners. These materials were later developed into hydrogels which were originally developed for their applications in the medical industry (Bruck (1973), Kazanskii & Dubrovskii (1992)). Hydrogels can be defined as three-dimensional polymeric networks that can retain a significant amount of water within their structures and swell without dissolving in water (Jamnongkan & Kaewpirom (2010), Guilherme et al. (2015)). By modifying the functional groups during synthesis, hydrogels could be adapted for use as soil conditioners. Soils that are amended with hydrogel show higher water retention. In most studies, an increasing concentration of hydrogel shows higher water retention in soils (Demitri et al. (2013)). Hydrogel can act as a water reservoir for plants, and its slow-release properties can be used to supply micro and macro nutrients to enrich the soil (Jamnongkan & Kaewpirom (2010)). Its degradation products can be engineered to improve the nutrient content of the soil, and thus promote the growth of symbiotic organisms in the soil (Abd El- Rehim (2006), Devineni et al. (2013)). The advantages and limitations towards sustainability associated with the use of hydrogel with respect to plant growth, and interactions with microbiome, soil and water are presented in this study.

Classifications of Hydrogel

Classification is necessary for a focused study of any material. Several hydrogel classifications have been documented by researchers (Kazanskii & Dubrovskii (1992), Ahmed (2015), and Ghobashy (2020)). The hydrogel classifications based on source, synthesis, crosslinking, and pore size are discussed in this section.

Classification based on Source

Hydrogels are formed by the crosslinking of polymers that are either naturally occurring or synthetically produced. The source-based classification is shown in figure 1. The earliest hydrogels used for agricultural purposes were synthetic, such as polyacrylamide, polyvinyl alcohol and polyethylene oxide (Kazanskii & Dubrovskii (1992)) which later were realized to pose potential environmental hazards (Zhang et al. (2014)). The synthetic hydrogels are known to possess high swelling degree, high durability, and slow degradation (Ahmadi et al. (2015)). Natural polymer-based hydrogels however have a low structural strength and a low swelling degree. However, natural-polymer based hydrogels are biodegradable (Ahmadi et al. (2015)). In some cases, the degradation products even enrich the soil. To combine the advantages of both natural polymer-based hydrogel and synthetic hydrogel, the natural polymers can be crosslinked onto synthetic polymers, giving rise to a new set of hydrogels.

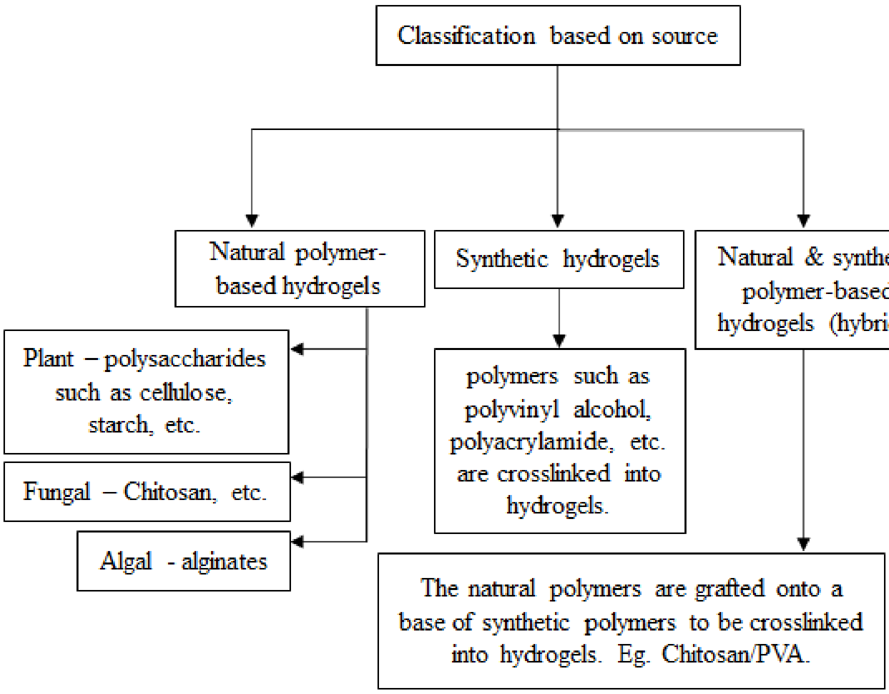

Figure 1. Source-based classification of hydrogel (Ghobashy (2020)).

For agricultural applications, cellulose based hydrogel is prepared from its derivative - cellulose ethers which show biodegradability, and non-toxicity (Ghobashy (2020)). carboxymethyl cellulose and hydroxyethyl cellulose (Montesano et al. (2015), Cannazza et al. (2014)) are examples of cellulose ethers. Novel hybrid hydrogels based on starch, chitin, tulip extracts have shown promising results in terms of swelling and degradability (Xiao et al. (2017), Kollar et al. (2016), Zhang et al. (2014)).

Classification based on Synthesis Method

Several synthesis methods of hydrogel have been reported in literature. Potentially, any polymerisation technique that produces crosslinks could be incorporated into hydrogels preparation. Specifically, solution polymerisation, graft polymerisation, radiation induced radical polymerisation, bulk polymerisation, and inverse suspension polymerisation are widely used and considered as a broad methodical classification as shown in figure 2 (Ahmed (2015)). Grafting to support polymerisation is discussed in detail in by Latif et al. (2016). They made attempts to combine chitosan-based hydrogel with PAAm, and PVA (polyvinyl alcohol). Solution polymerisation is well described by Kollar et al. (2016), where homopolymerisation, and copolymerisation are carried out with a compound known as tulipalin A (tulip extract derivative). Bulk polymerisation results in the formation of a single large matrix which can be prepared in the desired shape (Ahmed (2015)). Radiation induced crosslinking is done by irradiating the monomer units with high energy radiation such as gamma rays, X-rays, and electron beams. A study by Katayama et al. (2006), used Acacia senegal seeds for preparing hydrogel by using electron beams of different strengths. The method of synthesis and the concentration of crosslinking agents and initiators involved in the chemical reactions determine the resulting properties of the hydrogel such as swelling degree, resistance to temperature, and response to pH Guilherme et al. (2015), Ahmed (2015)).

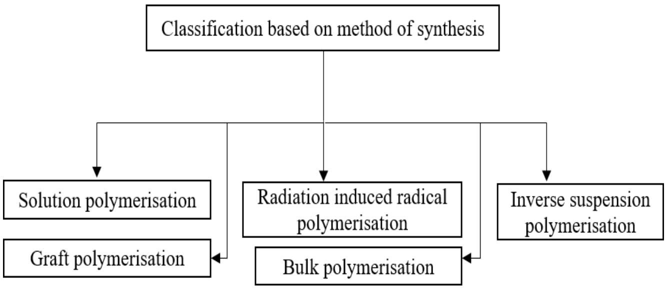

Figure 2. Synthesis methods (Ahmed (2015), Kazanskii & Dubrovskii (1992)).

Classification based on Crosslinking

Crosslinking is a key factor that enables the polymers to form three dimensional matrices which are elastic in nature allowing swelling as well as providing stability to the structure of the matrix. The classification based on crosslinking is shown in figure 3. Chemical crosslinking is permanent and gives strength and durability to the hydrogel. This is an advantageous property for applications under high temperature, varying pH, and pressure. Physical crosslinks are reversible because of its ready response to destabilize under external environmental stimuli. This is a limitation of physical crosslinking. However, the response to external stimuli is an advantage for the hydrogel to be used as a smart material in various applications such as moisture sensors and pH sensors (Shin et al. (2010), Tellis et al. (2011)). The swelling degree of the prepared hydrogel is mainly based on crosslinking density in a given unit of hydrogel matrix. Since higher crosslink density means lesser length of polymeric chains, and lesser elastic limit, swelling degree is inversely proportional to the crosslink density (Guilherme et al. (2015)). This is discussed in detail in section 3 of the review.

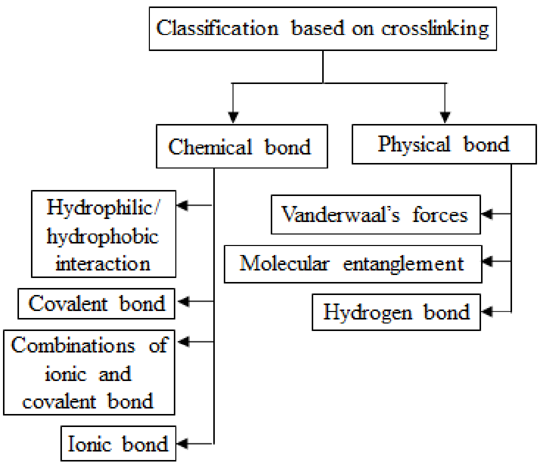

Figure 3. Crosslinking modes (Ahmadi et al. (2015)).

Classification based on Pore Sizes

Pore size is an important property in hydrogels used for drug delivery and has been dealt in detail by respective researchers Ahmed (2015), Omidian et al. (2005), Ahmadi et al. (2015). The classification based on pore sizes is shown in fig 4. In agricultural, the swelling rate is not the governing factor for application. Rather, swelling ratio, slow-release kinetics, and biodegradability are considered during synthesis. Thus, a glassy matrix with absorption of a few hours (Parthasarathi et al. (2018)) can still effectively deliver in soil for agriculture.

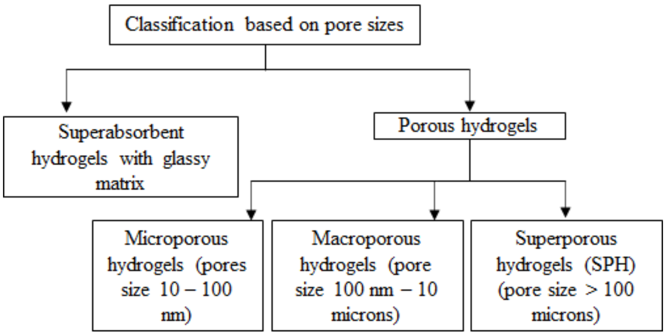

Figure 4. Pore-size based classification (Chen et al. (1999)).

Stimuli Responsive Hydrogel

Stimuli responsive hydrogels (SRH) are a class of smart superabsorbent polymers that change one or more of its properties as a response to a particular change of any of the environmental parameters such as temperature, overburden pressure, pH, ionic concentration, osmotic pressure, and electromagnetic field (Rehman et al. (2011)). Ahmed (2015) mentions SRH that can be applied in biological, and physical processes for a variety of applications. Advances in SRH are mainly developed into biosensors for drug delivery, textiles, and micro electromechanical systems (Stuart et al. (2010)). Biocatalytic systems coupled with hydrogel membranes that deliver specific enzymes in response to biochemical signals and reactions facilitates fast drug delivery and transport (Tokarev et al. (2009)). A good photonic crystal hydrogel is one which undergo a change of colour in response to change in pH. An interpenetrating photopolymerized hydrogel showed a colour change within 10 to 20 seconds for pH ranging from 3 to 6 (Shin et al. (2010)). The absorption of water by hydrophilic polymers in the hydrogel matrix could be used in monitoring the water content of the surroundings. Such a sensor is mentioned in recent literatures. Agarose based hydrogel films incorporated with dapoxyl sulfonic acid (fluorophore) changed over a range of 30 to 40 nm wavelengths for a 0 % to 100% change in air humidity and gaseous medium with a 15-minute response time (Tellis et al. (2011)). Tellis et al. (2011) points out that the use of environment sensitive fluorophore rather than the polymer chains or crosslinkers for detection of environment change enables the incorporation of this property into a variety of hydrogels to be used as smart materials. This opens the scope for studies that can exploit the properties for agricultural applications such as moisture-based release systems, time-based fertilizer release systems, and enzyme-based pesticide/fungicide systems.

Properties of Hydrogel

Ideal Properties for Agriculture

It has been highlighted that the traditional forms of irrigation in India, such as check basin and furrow types, failed to perform in a sustainable manner, as they induce wastages such as evaporation losses, and losses of nutrients from fertilizers due to leaching, to list a few (Parthasarathi et al. (2018)). The properties of hydrogel considered in this section largely pertain to characteristics mediation of which would effectively improve soil and agriculture performance. The categories were chosen on the basis that water and nutrient delivery should be optimized, while the effective use of hydrogel over the field should be reduced, to save resources in the form of water, fertilizers and capital. The characteristics of hydrogel for agricultural applications could be drawn as follows (Ahmed (2015), Neethu et al. (2018)):

- The swelling degree must be high enough so as to reduce the application of superabsorbent polymer (SAP). The swollen size of the hydrogel must not hinder the aeration pores of the soil structure. Thus, a compromise in the swelling degree of hydrogel must be made to ensure that there is no detrimental effect on the aeration pores.
- The structure of hydrogel must withstand the mechanical pressure from the soil and pore water surrounding it. Synthetic polymers provide durability, as the degradation of synthetic polymers is low. Thus, a partnership between the use of natural polymers for degradability and eco-friendliness, and synthetic polymers for durability for the required time must be made.
- The hydrogels must be capable of slow release of water and fertilizers. The slow release must be predictable to control the management of water for optimization. The nutrient release must adhere to a predictable fashion irrespective of environmental changes.
- The hydrogel must act as bio inoculants that enrich the microbial population that contribute to symbiosis is the soil.
- The hydrogel must be biodegradable. The degradation products should bear no toxicity to the biota. The degradation products should enrich the soil fertility.
- In view of this, the properties of swelling, slow release, impacts on soil-plant-microbe, and degradation of hydrogel are discussed in this review. As seen earlier in section 2.2 and 2.1, the properties and behaviour of hydrogel are mainly dependent on the material with which it is made, and the process of synthesis. Cellulose based hydrogel prepared from free radical graft polymerisation of acrylamide and acrylic acid onto cellulose from mulberry branch extract shows a swelling degree of 500 (Zhang et al. (2014)). Cellulose based hydrogel prepared from solution copolymerisation of carboxymethyl cellulose/Na showed a maximum swelling degree of about 200 (Sannino et al. (2010)).

Adopted assays for quality assessment of hydrogels are as follows:

- Encapsulation efficiency: The test is carried out to determine the amount of fertilizer encapsulated in the hydrogel with respect to the amount of fertilizer dissolved during synthesis. (Jamnongkan & Kaewpirom (2010)) uses the equation 1.

$$\eta = \left[1 - \frac{\gamma'}{\gamma}\right] \times 100 \qquad (1)$$

where γ' is the unencapsulated amount of fertilizers, γ is the total amount of fertilizers, and η is the encapsulation efficiency.

- Fertilizer release in water: 75 ml of water is dissolved with controlled release fertilizers (CRF) and 30 ml of water is taken out for testing every 24 h, for atomic absorption spectrophotometry to obtain the amount of potassium in the sample. Additional 30 ml is added to it to maintain water availability (Jamnongkan & Kaewpirom (2010)).
- Water absorbency: There are different methods to determine the water absorbency or swelling (times) or swelling degree (%). Jamnongkan & Kaewpirom (2010) and Latif et al. (2016) both reported the following method: The dry hydrogel is weighed and immersed in deionised water. At regular time intervals, the swollen hydrogel is taken out, wiped gently on the surface with tissue/filter paper to remove excess water, weighed and re-immersed in the water. The formula used is 2.

$$\text{Degree of Swelling SD\%} = \frac{W_s - W_d}{W_d} \times 100 \qquad (2)$$

Where W_s is the swollen weight and W_d is the dry weight of hydrogel (Jamnongkan & Kaewpirom (2010), Latif et al. (2016)).

- Water retention in soil: 100g of soil is taken in two vessels of known weight each, one with hydrogel and the other without. The amount of water poured in them should be same and should be kept under identical conditions. The weight of the soils is taken in regular intervals (24 hours) for 30 days (Jamnongkan & Kaewpirom (2010)). Percentage water content in each day is calculated to get the moisture release curve.
- Water holding capacity of soil: Several pots are filled with measured amounts of soil, with different concentrations of hydrogel, and one without hydrogel (control). Water is filled until percolated water comes out through the holes. Re-watering is done thrice to ensure maximum swelling of hydrogel. The formula used is water holding capacity (WHC) is as given in equation 3.

$$\%\text{WHC} = \frac{W_s - W_d}{W_d - W_p} \times 100 \qquad (3)$$

Where W_s is weight of a pot with water saturated soil, W_d is weight of a pot with dried soil, and W_p is weight of pot without soil (Rychter et al. (2019)).

Chitosan hydrogel has high biodegradability and low swelling due to low relaxation rate of polymer chains. A study done by Jamnongkan & Kaewpirom (2010) compared the swelling of hydrogel produced by only PVA (synthetic), PVA/Chitosan blend, and only chitosan (natural); the results showed that swelling was of the order PVA>PVA/CS>CS. A blend is necessary to incorporate biodegradability and high swelling. For their success under Indian conditions, the key requisites include their workability in harsh tropical and subtropical climates, particularly with respect to higher temperature conditions, and a sustained release of water from their matrices for use by plants. Re-wetting capability, if required, the hydrogel has to be able to give back the imbibed solution or to maintain it; depending on the application requirement (e.g., in agricultural or hygienic applications) (Ahmed (2015)).

Swelling Properties

Swelling refers to the property of the hydrogel to retain water as a virtue of its crosslinking and hydrophilicity. As these hydrophilic groups helps hydrogel to absorb water molecules which in turn expands the 3D matrix, this is also known as swelling. The Degree of swelling therefore can be attributed to the number of linkages that the particular hydrogel harbours (Jamnongkan & Kaewpirom (2010), Ahmadi et al. (2015)). The swelling of the polymerized gum arabic was estimated according to the Japan Industrial Standard (JIS) K7223. The initial dry weight of the hydrogel is measured, and immersed into the solvent for a 16–24-hour period (for maximum swelling). Subsequently the hydrogel is drained through a mesh (the pore size varies from 80 - 150 micrometer). Weight of the final residue is measured and equation 2. Swelling properties measured as a function of time can be measured using the equation 4

$$\eta_t = \frac{\sigma_{t=0} - \sigma_t}{\sigma_{t=0}} \times 100 \quad (4)$$

where the $\sigma_{t=0}$ is the initial concentration of the solute without the hydrogel, and σ_t is the final concentration after a set period of absorption of the selected hydrogel (Guilherme et al. (2015)). This may provide an insight into the initial response of hydrogel in the solvent and could be a preliminary assay to check the loading capability or, in this case, swelling (Guilherme et al. (2015)). Fumio et al. (1990) and Ahmadi et al. (2015) also derives the swelling ratio as a function of inverse proportion of its cross-linking density upon polymerization, with the explanation that the presence of larger spaces within the hydrogel structure helps it hold greater amount of water in the empty pockets. As the cross-linking in the matrix intensifies, the Poisson's ratio reaches 0.5. It causes a reduced swelling degree of the matrix (Pritchard & Terentjev (2013), Körner et al. (2009), Paul et al. (2014)). To measure the degree of cross-linking or effective cross-linking density can be formulated using Flory and Rehner's equilibrium swelling theory 5.

$$[\ln(1 - V_2) + V_2 + \chi V_2^2] = \frac{V_1}{V \cdot M_c}\left(1 - \frac{2M_c}{M}\right)\left(V_2^{\frac{1}{3}} - \frac{V_2}{2}\right) \quad (5)$$

Where V_1 and V_2 are the volume fraction of solvent and polymer in the matrix, x is the Flory solvent-polymer interaction parameter, $V^{\,l}$ is the specific volume of the polymer, M

is the primary molecular weight of polymer (before the crosslinking process) and M_c is the average molecular mass between crosslinks or the network parameter (Guilherme et al. (2015)). The ability of hydrogel to swell or shrink can be controlled to an extent as they display drastic changes in this property as a response to external physical and chemical stimuli such as temperature, pressure, sound, pH, solvent composition, ionic strength and molecular species (Ahmadi et al. (2015), Fumio et al. (1990)). The importance of the polymer backbone with respect to the amount of hydrophilic functional groups it carried was explained by Murphy et al. (1992), by comparing homogeneous poly (acrylic acid) with 1% ethylene glycol dimethacrylate cross linking containing pendant carboxylic acid groups and homogeneous poly (2-hydroxyethyl methacrylate) polyHEMA at similar crosslink densities exhibiting equilibrium water capacities (swelling) at 73% to 38%, respectively.

Fumio et al. (1990) has also shown how the number of freeze-thaw cycles involved in the production of hydrogel also have an impact by ultimately changing the swelling potential. The amount of PVA not incorporated in the hydrogel decreased from 10.6% to 7.0% when subjected to 4 freeze-thaw cycles. The connections between the polymers also appeared much more rigid as the number of cycles increased, as shown through Scanning Electron Microscope (SEM) imaging. This also resulted in a noticeable reduction of swelling over increase in the number of cycles. Furthermore, the degree of swelling of the PVA hydrogel appeared to have a distinct correlation with reciprocal absolute temperature and increased almost linearly at most temperatures. Expansion of the polymeric chain or swelling can be credited to the phenomenon of migration of solvent molecules into the cross-linking polymer. Due to the increase in the solvent concentration inside the polymeric chain, mostly a cause of osmotic force, the ionic repulsion increases which consecutively aids in enlargement of the matrix. Polymeric chain, in opposition to the ionic repulsion, is held together by the elastic retractive forces. The maximum swelling occurs when the equilibrium state (i.e., the net force acting on the matrix becomes zero) is achieved (Guilherme et al. (2015)). As expansion of the polymeric chain depends on the water diffusivity, it is then basic to study the diffusion mechanics of water into the matrix. Using Fick's law of diffusion, the mass transfer is measured for a given period of time through a given medium/space. The following formula is the basic principle of Fick's diffusion law 6.

$$J = -K \times \frac{dQ}{dx} \quad (6)$$

where flux J is the Net rate of particles moving through an area, Gradient $\frac{dQ}{dx}$ is the change in pressure or concentration over a length and diffusion coefficient K is the ratio of Solubility to the square root of the molecular weight (Brazel & Peppas (1999)). A derivative of the aforementioned formula has been derived as an empirical relation to explain the diffusion kinetics is Korsmeyer-Peppas model (power law) 7:

$$\frac{M_t}{M_{eq}} = Ct^n \quad (7)$$

where M_t is the amount of water absorbed/nutrients released at time t, M_{eq} is the amount of water absorbed/nutrients released at equilibrium, C is the characteristic constant, n is the diffusion exponent characteristic of the absorption/release mechanism (Jamnongkan & Kaewpirom (2010)). Table 1 gives a brief on the type of diffusion in correlation with the value of the diffusion constant. Superabsorbent Polymers (SAPs) and Superporous Hydrogels.

Table 1. Range of values of diffusion exponent for different mechanisms of diffusion (Jamnongkan & Kaewpirom (2010))

Diffusion exponent	Diffusion characterics
n<0.5	Quasi-Fickian
n=0.5	Fickian
0.5<n<1.0	non-Fickian
n=1.0	Case II transport

(SPHs) are relatively newer classes of polymers. The main difference between these two lies in the diffusion mechanisms by which the water enters the hydrogel network. SAP and SPH both exhibit relatively very fast swelling properties upon the application of water, however the former is largely dependent on the size of the particles or samples in their initial dry states. As the diffusion constant is inversely proportional to the molecular weight of the solvent, the diffusivity of such particles has considerable difference. SPH overcomes this problem by the virtue of the interconnected open channels they have in their matrices which allow the water to flow in, regardless of the size of the sample. The pore sizes in SPHs range in the order of hundreds in their dry states (Chen et al. (1999)). Another difference observed was that, toward the end of the drying process where control over the final drying of SAP is very critical as it affects its final swelling properties, unlike the process for SPHs, where the polymerization process is limited to the time of gel formation (Omidian et al. (2005)). Latif et al. (2016) studies the swelling of differently prepared hydrogels over time, showing a distinct superiority of the equilibrium of a hydrogel prepared by graft copolymerization of acrylic acid (Pg) on PVA, explaining this phenomenon by the fact that the –COOH groups in hydrogel molecular structure acted as excellent hydrophilic groups, and thus facilitated higher concentrations of water inside in the matrix, also recommending that this required further research. Certain applications also required fast swelling of hydrogels, and these have been widely explored too. Chen et al. (1999) derived hydrogel for drug delivery whose fast swelling, preferably in 5 – 30 min. The tiny interconnected pore spaces behaved as capillary tubes (open channels) within the dry hydrogel matrix, which allowed the water to diffuse rapidly. This could be explained for SAPs as a two-phase process where water molecules are first accumulated on the outer layer, creating a state of duality of dry hydrogel and partially swollen. Water continues to diffuse into the hydrogel pores towards its centre. SPHs bypass the first process due to the continuous movement of water through its channels immediately, resulting in faster swelling (Omidian et al. (2005)). Many studies have indicated a change in equilibrium swelling potential over hydration and rehydration cycles, mostly notably in agriculture related studies. This could be attributed to the increasing salinity of water, due to fertilizer and soil-water salt interactions, being absorbed by the hydrogel themselves (Cannazza et al. (2014), Demitri et al. (2013)). Division in the H- bonds due to low pH, resulted in increased swelling degree in chitosan-based hydrogel (Jamnongkan & Kaewpirom (2010)).

Water Retention Properties

For agricultural purposes, an ideal hydrogel would ideally be averse to degradation and hold water under loading conditions and for longer periods of time, in order to deliver water to the plant root hairs only under the latter's potential. This is one reason SAPs are used in agricultural facilities as the amount of water retained under pressure is relatively exceptionally high (Omidian et al. (2005)). SAPs prepared as nonporous hydrogels find remarkable applicability in agriculture as this property also imparts mechanical stability to the polymer and prevents breakdown under sustained soils loads when dispersed in it (Omidian et al. (2005)).

To determine the capacity of the SAP to act as soil conditioner, the SAP samples are submitted into an environment in which the difference in pressure between the soil and the root of vegetables is simulated. A way of doing this is to measure the water uptake at different pressures. The hydrogels are added into a vessel with Richard membrane-covered walls. The water is withdrawn from hydrogels by increasing the pressure of the vessel. The data of water content can be obtained as a function of water retention (given in kg water per kg hydrogel) under pressure given in hecta Pascal (hPa) (Guilherme et al. (2015)). The release kinetic can be changed by adding inorganic particles into hydrogel. The particles, when sufficiently dispersed, cause a tortuosity effect that disturbs the release of solutes. Such an effect gives longer pathways that difficult the diffusion of the solute toward the outside hydrogels. The particles play a role as a retardant factor for drug release (Guilherme et al. (2015)). Studies have however shown exceptional advances in this specific trait. Chen et al. (1999) developed hydrogels for oral drug delivery that showed resilience for 24 to 60 hr in canine stomachs.

Experiments conducted by Cannazza et al. (2014) show the water retaining capability through its release of a synthetically manufactured hydrogel swollen with tap water to be higher after the 5th day than distilled water, speculating that the fixed electrostatic charges on the polymer network. The presence of mineral clay on hydrogels without the hydrolysis treatment, delayed the nutrient (e.g., urea) desorption in quite a significant way. However, an important factor was that, for the hydrolyzed hydrogels, desorption time and the amount of nutrient desorbed increased significantly (Guilherme et al. (2015), Ismail et al. (2013)). As reported in a study focused on the same class of hydrogel used in the present research, the hydrogel swelling is reduced with increasing electrical conductivity; therefore, we can expect a reduced ability to improve the water retention capacity of the substrates in actual cultivation conditions, especially when the substrate electrical conductivity tends to increase with the progress of the crop cycle (Montesano et al. (2015)).

Slow-release Properties

Studies indicate that the dominant contributor for surface water eutrophication and groundwater nitrate enrichment is the uncontrolled release of agricultural nutrients, herbicides and pesticides on soils. The most crucial and indispensable nutrients for planting soils include potassium, calcium, iron, copper, nitrogen, phosphorus, sulfur and boron, although it is estimated that around 40 - 70 % of nitrogen and 50 - 70 % of potassium are lost by leaching. High quantities of nutrients are not absorbed by plant roots. Thereby, the main aim of using coated fertilizer granules and crosslinked chemically polysaccharide-based hydrogels in the controlled nutrient release on soils is the decreasing the loss of nutrients by leaching and mitigating environmental problems (Guilherme et al. (2015)). Moreover, the use of controlled release fertilizers causes an increase in their efficiency, reduces soil toxicity, minimizes the potential negative effects associated with overdosage and reduces the frequency of the application. Two methods, post and in situ loading have been reported for the loading of nutrients onto the polymer matrix. The in-situ approach is preferred over post-loading one because of the greater loading efficiency. Jamnongkan & Kaewpirom (2010) reported a high efficiency of more than 99% for in-situ loading. The water within the hydrogel dissolves the nutrient, which can diffuse through the polymer network. The movement of solutes toward the outside of the hydrogel can be related with swelling rate. Only a small amount of the load is released. As a result, a portion of loaded solute is preserved when the hydrogel dries in the intervals of irrigations or rains. The release is again activated in the further watering processes, thus providing a prolonged release process that can prevent the leaching. It is also possible to load two or more active substances onto hydrogel so that each one of them may have specific release kinetic. The fraction of nutrient, herbicide, pesticide or other solute released from chemically crosslinked hydrogels may be calculated as given in equation 8 (Guilherme et al. (2015)):

$$Fraction\ release = \frac{Amount\ released}{Amount\ loaded} \quad (8)$$

The release profiles from coated granules are divided in three main steps: i) initial stage with no significant nutrient release, ii) constant release from medium intervals, and iii) gradual decay of the release rate from the longer release period. A mathematical model based on Fick's second diffusion law, based on the nutrient release profiles as a time function, was developed to predict the release rate of polymer-coated fertilizer using a numerical solution and Fourier series expansion. The release time t' during the initial stage was defined by the equation 9

$$t' = \frac{(\gamma r l)}{3P_h \Delta P} \quad (9)$$

where y is the total granule porosity including also voids between the nutrient core and the membrane; P_h is water permeability of the membrane (in $mm^2\ Pa^{-1}\ Day^{-1}$); P is the vapor pressure difference between water and saturated nutrient solution (in Pa); and r is radius of diffusion (in mm) in the coated granule (Guilherme et al. (2015)). The nutrient release process is attributed to the diffusion behavior of the hydrogel itself, where the fertilizer is encapsulated within a water medium inside the hydrogel, and is released alongside it when the hydrogel starts de-swelling, as illustrated by (Ghobashy (2020)). It has also been insinuated that Smart Biodegradable Hydrogels are used to coat fertilizer in order to control the release of nutrients, which vary according to certain parameters themselves, like the temperature of the media, observing a higher release for increasing temperatures. Pure polysaccharides degrade very quickly in soil, and therefore cannot be used as nutrient carrying vehicles (Zhang et al. (2014)). Therefore, they are processed to make semi-synthetic hydrogels, as discussed earlier. Natural polymers such as starch and cellulose are used to coat fertilizer granules such as Urea in order to make slow-release nutrient derivatives (Ghobashy (2020)). Hydrogel coatings that release only 15% of the total Urea after 1-2 days of application have also been derived, in order to minimize undesirable fertilizer leaching into the soil (Zhang et al. (2014)).

Soil - hydrogel Interaction

Impact on Soil Properties

Hydrogel improves the water retention of soils in arid and semi-arid zones, and supplements agriculture by increasing the amount available in the root zone depth to plants, further increasing the amount of time between successive irrigations. Soil - water relationships are quantified by parameters such as soil water potential, soil water capacity (SWC), available water capacity (AWC), and readily available water capacity (RAWC). Soil water capacity could be calculated from the guidelines given in IS 2720 (1983) and other standards. The available water capacity of soil is calculated from the amount of water removed from suction between the pressures of 30 kPa and 1500 kPa. The readily available water capacity of soil is measured from the difference in water content at 10 kPa and 100 kPa (Narjary et al. (2012)).

In a study done by Narjary et al. (2012), different types of soil were treated with 0.4% and 0.7% hydrogel by weight. The AWC and RAWC water for the control group of the soils and the treated soils were measured. In all, the values of SWC were highest for the 0.7% mix of hydrogel and soil. The hydrogel treated soil reached critical soil water capacity only after 22 days in sandy soil (Narjary et al. (2012)). In a study by Agaba et al. (2011), the water retention was so high that for a period of 69 days, the soil required watering just once in the beginning to sustain the grass species Agrostis Stolonifera. Montesano et al. (2015), have shown how the application of 1-2% w/w of hydrogel in sandy soils (91.5% sand, 4.2% silt and 4.3% clay) had a very positive impact on it by doubling, and even quadrupling the soil water holding capacity, making it comparable to even silty clays and loamy soils (Katayama et al. (2006)). Rychter et al. (2019) showed through experimental analysis of soil-water-hydrogel setup by conducting water holding capacity test and water retention test. The results from this study by Rychter et al. (2019) show significant increase in the water holding capacity of soils with high hydrogel content (0.1% w/w), and the water retention was at least thrice that of the soils without hydrogel. Soil conditioners based on naturally occurring polymers such as guar have been shown to prevent surface crusting of soil (Wallace (1986)).

Hydrogels provide the soil texture and porosity necessary for optimum air and water flow in the soil, and release the stored water when the soil is dried up. All of this facilitates the maximum growth potential for plants (Guilherme et al. (2015), Ghobashy (2020)). This is partly due to the fact that leaching of water through gravity in the soil particles is partially suspended by the swollen hydrogel particles in the voids of the soil. It is known that the soil porosity is not affected unless the size of the swollen hydrogel particles or clusters are in the range of centimeters (Chen et al. (2004)). The porosity of soil should not be less than the critical value of 10% for plant growth (Narjary et al. (2012)). However, minimal use of hydrogel is advised for soils with high moisture retaining capacities, as it may hinder plant root aerobic interactions (Parthasarathi et al. (2018)). The presence of hydrogel increases the soil porosity that provides a better oxygenation to the plant roots (Guilherme et al. (2015)).

Field level experiments have been done by Abrisham et al. (2018) by the use of a potassium polyacrylate based hydrogel - stockosorb on S. rosmarinus Bunge ex Boiss. (Amaranthaceae) for the evaluation of effects on properties of sandy loamy soil and plant growth. The study by Abrisham et al. (2018) showed a decrease in infiltration capacity, increase in cation exchange capacity and a decrease in bulk density. In many areas, particularly in Egypt, hydrogels are being experimented upon as a utility to ameliorate the effect of extremely saline soils on plant growth, caused due to irrigation with saline water and poor permeability and drainage, to list a few (Chen et al. (2004), SAYED et al. (1991)). SAYED et al. (1991) indicates a decrease in ionic uptake from saline treatments due to reversal of ionic osmotic exchange between plant-soil-hydrogel chains. Chen et al. (2004) showed that the water content of saline soil amended with hydrogel increased by 41%. Moreover, the saline concentration of the soil was reduced in soils amended with hydrogel.

Hydrogel Impacts on Microbial and Fungal Growth

Microorganisms in the soil matrix play a crucial role in the nutrient pathway for plant uptake. Many bacteria and other single and multicellular species break down the complex nutrients inside the soil and release it to the roots of the plants in its vicinity. A plant root system has a complex interaction with its environment such as rhizobium fauna, fungi, and bacteria. Hence, a healthy population of nitrogen and other nutrient fixing bacteria is tantamount to optimizing the overall yield of the plant (Jacoby et al. (2017)). This ecosystem is important for a sustainable environment for plant growth as this combination in the ecosystem ensures a natural equilibrium between nutrient transfer and survival of each species. As most of these organisms propagate in aqueous situations, the availability of moisture in the form of entrapped water in hydrogels help create incubation tanks for the same.

The interaction of microbes with hydrogel involves complex reactions and exchange of enzymes. The microbes are exposed to nutrient release and degradation products of hydrogel. Since symbiosis is essential for plant growth, hydrogels applied for agricultural productivity should pose no toxicity to the symbiotic organisms. The hydrogels thus require to be tested for any sort of negative effects on microbes.

Cytotoxicity test, and high through-put genome sequencing of soil microbes are popular methods adopted for the evaluation of the effect of hydrogel on microbial communities (Rudzinski et al. (2002), Sannino et al. (2010)). Cytotoxicity test used to measure the extent of damage which the hydrogel, its extract, or its monomers can cause on a living cell and is done using a colorimetric assay based on MTT, a tetrazolium salt (Mosmann (1983)). The test compares the cell viability as a function of concentration compared with Polyethyleneimine (PEI) as control (Kollar et al. (2016)).

A study done by Rudzinski et al. (2002) mentions the use of a genome sequencing method called Illumina MiSeq sequencing, where the genomes of existing microbial communities are measured in soils in the presence of Sodium polyacrylate hydrogel under 4 different conditions of soil moisture. The study by Rudzinski et al. (2002) showed that the diversity of microbes increased with the addition of SAPs and that soil moisture content played a greater role in deciding the degradation of SAPs. Saturated water treatment showed a release of toxic compounds, while severe drought treatment showed a decrease in pH. This discourages the use of PAAm based hydrogels for agricultural purposes. However, polyacrylate-based PUSA hydrogels were used as bioinoculants in a study done by Suman et al. (2016) where the shelf life of microorganisms was boosted from 3 months to 2 years in controlled conditions and the treatment of the select cultures of microbes and hydrogel showed positive effects on plant growth. Although positive effects are observed in the immediate crop production as shown in many studies, the toxicity at longer time periods after degradation requires to be given sufficient scrutiny. Considering the uncertainty projected here, the effects of toxicity of natural polymer-based hydrogels needs to be studied in detail. Starch based hydrogels undergo fermentation, producing sugars, which serve as food for many microbe species. The total microbial count for Actinomycetes, Azotobacter, total fungi, phosphate dissolving bacteria, and Azospirillum progressed when applied to sandy calcareous soil (El-Hady et al. (2011)). Kollar et al. (2016) used MTT assay for AM-SHMB (tulipalin A based) hydrogel, its monomers and extract and found that AM-SHMB doesn't cause toxicity to the cells, or doesn't damage the viability of the cells for 3, 5, and 10 mg/ml of concentrations. Genome sequencing on the other hand is only recently used for agricultural purposes. Another study, by Sannino et al. (2010) showed through MTT assay, that cellulose-based hydrogels have no toxicity towards cell viability. A study by Achtenhagen & Kreuzig (2011) showed that there is an increased microbial activity with the application of hydrogels under deficit conditions. Many microorganisms contribute majorly to the degradation of the hydrogels themselves, and promote microbial survival. Ghobashy mentions the desirability of aerobic bacteria in soils that fix oxygen to the root systems, and discusses the converse of the anaerobic type, citing their parasitic nature that often leads to competition between the plant and the bacteria themselves for mineral nutrients and nitrogen, leading to diminished plant growth (Ghobashy (2020)).

Hydrogel Impact on Plant Growth

It is important to examine the effect of the altered soil water interactions due to the application of hydrogel on the growth of the plant themselves. A large number of studies have been carried out in this regard in the field of Agronomy. Hence, a sufficient number of results are available to compare the standard methods of cultivation with those that have been augmented with the use of hydrogel, based on a variety of plant growth parameters. The hydrogel is applied to the plants by different methods: either seedlings or seeds are coated with hydrogel, or hydrogel is mixed with the soil adjacent to the sown plants (Kazanskii & Dubrovskii (1992)). The hydrogel binds strongly to the roots of the plants in many cases, and thus enhances the nutrient environment around them. However, the methods can prove counterproductive, as the swollen hydrogel has the chance of blocking soil pores required for aeration resulting in seedling mortality (Ghobashy (2020)). In general, hydrogels have shown to be largely favourable when used to aid cultivation. There are no reported phytotoxicity cases, notably manifested through increased germination indices of many vegetables as well as ornamental species when treated with hydrogels. Trials on cucumber showed an overall increase of over 30cm in plant height, as well as increasing the plant and fruit fresh biomass (by weight) almost twofold (Montesano et al. (2015)). Since the production of chlorophyll is linked to water availability, plants growing in soils without hydrogels have shown significant decrease in chlorophyll content as compared to when hydrogel is applied in soils. Plant defenses against diseases have also been shown to be increased by the action of hydrogel, curbing the actions of a variety of phytopathogens, as well as inhibiting the growth of nutrient intensive fungi species (Ghobashy (2020)). Chen et al. (2004) observed 3.5 times increase in root length and area of tree seedlings when saline (Potassium mine refuse) soils was amended with hydrogels. Since vitality of the plants grown is generally quantitatively measured with respect to certain established independent parameters, this section will try to combine findings from different studies performed on the plants. Plant parameters generally measured as an indicator of its growth potential includes, but are not limited to:

- Water Use Efficiency
- Dry Biomass Weight
- Number of days to Wilting point
- Germination Index
- Root length/surface area
- Shoot length
- Chlorophyll content
- Plant height
- Turgor potential
- Yield weight
- Leaf Water Content

- ***Impact on plant species***
  - ***Maize***

Higher seedling growth for Zea mays cv. 'tri-hybrid 311' in sandy soils in Egypt was observed for higher consequent concentrations of hydrogels added, with 0.4% having the highest growth recorded. Water content of the root and shoots showed an increase of at least 19% and goes to around 50% and even 70%, yielding higher average values for higher concentrations of hydrogel. An increase of fresh weight up to 1.56 to 7.9 times was also observed compared to its respective control (Mazen et al. (2015)).

- ***Tomato***

Levels of Chlorophyll A and B doubled for Lycopersicon esculentum Mill. species of tomato when Cross-linked Poly (ethylene oxide) co-polyurethane hydrogel was applied to the extremely saline sandy soils they were planted in. This was also accompanied by a consistent increase in photosynthetic activity, measured as a degree of O_2 evolution, in the same trials (SAYED et al. (1991)). Tomatoes (Pomodoro di Morciano di Leuca) were tested over 3 months in the Mediterranean region (province of Italy) with cellulose based SAP in red and white soils. Initially tomatoes were kept in pots and subsequently transferred to large wooden boxes to mimic open field condition. Differing concentrations from 0.2% to a maximum of 1.5% of the SAP was applied to the surface of the soil in each box, and only half the amount of water was supplied to the boxes containing SAP compared to the ones without (120L of water to non-SAP vs 60 L to SAP). The 0.2% hydrogel and control groups bore smaller and wrinkled leaves compared to the rest of the groups with higher SAP concentrations, even with the massive reduction in the amount of water supplied to the latter. The fruit size remained approximately the same (Demitri et al. (2013)).

- ***Cherry Tomato***

Cellulose based hydrogel with 4 concentrations up to 1% by wt. were mixed into red soil to assess its effect. It was initially observed that the plants reached their wither point when their respective soils reached a water content of 10-20%. Based on this, the control group was shown to take only 4-5 days to reach this stage. An addition of just 0.2% hydrogel increased this to 9 days, while the maximum concentration of 1% increased that further to around 22 days to wither (Demitri et al. (2013)).

- ***Populus Euphratica***

Plants treated with 0.6% Stockosorb K 410 hydrogel showed a 2.7 times biomass increase over control in saline conditions, over a test period of 2 years. Root length and surface area were also reported to increase 3.5 times (Chen et al. (2004)).

- ***Wheat***

Studies were conducted on wheat (Triticum aestivum L.) irrigation aided with lignite, liquids and hydrogels to assess their microbial and plant growth. Pusa hydrogel used in the experiment reported the highest root and shoot length, as well as the highest fresh and dry weights at 45 and 90 DAS (Suman et al. (2016)). Studies done in sandy calcareous soil from Egypt on the effect on 4 different types of hydrogels also examined its effects on the rhizosphere of the same species of wheat, concluding that it helps increase in growth promoting bacteria, and also boosts enzymatic activity in the plant surrounding. Applications of 2.5g/kg of hydrogel in the soil showed better results for the same as compared to 5g/kg, increasing the phosphate dissolving bacteria, total fungi and actinomycetes count to around 200% that of the control (El-Hady et al. (2011)).

- ***Cucumber***

Researchers showed the ability of a cellulose-based hydrogel to increase the germination indices of radish, cucumber, Alyssum, and Centaurea seeds well above the required 60% (set as a benchmark for signs for phytotoxicity), with cucumber trials reaching upwards of 140%. Pot cultivation trials done of the same showed similar positive results at 35 days after transplant, with 113% increase in plant height, 192% increase in total fresh biomass, 242% increase in fruit biomass, and 162% increase in leaf area. They also expressed higher leaf water potential and turgor potential values when subjected to controlled water stress (Montesano et al. (2015)). In addition, studies done by SAYED et al. (1991) also showed growth of cucumber in extremely saline solution concentration soils of up to 32,000 ppm with the addition of hydrogel, which would be otherwise previously severely impeded in the absence of hydrogel.

- ***Basil***

It has been observed that there was 156% increase in fresh weight at 46 DAS was found for perlite amended with 3% cellulose-based hydrogel as opposed to unadulterated perlite. This number is increased to 177% when 6% hydrogel concentration is used instead. However, this difference becomes less drastic at 63 DAS, showing only a 113% increase in the same parameter (Montesano et al. (2015)).

- ***Brassica Rapa***

0.15% SAP powder used to amend potted soil with fertilizers was shown to give 10% extra yield compared to control over three cycles of sowing and harvest over 30 days. This is significant as no extra hydrogel is added after the first incorporation into the soil, and can potentially use as an indicator of the reusability of the hydrogel itself (Shimomura & Namba (1994)).

- ***Lettuce***

Studies conducted by Woodhouse and Johnson on Lactuca sativa (cv. 'Webb's Wonderful') showed a significant jump in the number of days to wilting point from 2 in control to 15 days for sandy soils amended with PVA hydrogel at the max concentration of 0.5% w/w. Dry weight of lettuce increased six-fold under addition of Polyacrylamide hydrogel from 8 mg per pot to 49 mg per pot of sandy soil. Water use efficiency, another excellent indicator of plant growth efficiency, also had 3-fold growth over its respective control in the experiment (Woodhouse & Johnson (1991)).

- ***Agrostis Stolonifera***

Experiments done on this species of grass in pots with sand from a sand pit in Schoningen, Germany with 0.4% Luquasorb hydrogel showed an increase in the root and shoot biomass measurements by 4 and 2.2 times, respectively. The water use efficiency also was observed increased by 8 times from 1.56g/L to 13.7g/L. The total amount of water used was also lessened by 3 times from 24L in control to 8.4L in 0.4% hydrogel concentration (Agaba et al. (2011)).

- ***Faba bean***

The effect of irradiated polyacrylamide and PAAm/Na-alginate copolymer hydrogel was assessed with the help of the growth of faba bean (Vicia faba L. Family: Leguminosae) in semi-potted sandy soil in Egypt and showed clear higher biomass and plant height measurements at 9 weeks after sowing (Abd El-Rehim (2006)).

Hydrogel Degradability

Non degradability of most synthetic hydrogels can pose environmental threat. The problem of degradation arose with extensive application of hydrogel polymers in the medical industry. Two ways for the degradation of synthetic polymers were identified - introduction of functional groups in the crosslinks of hydrogel that can undergo hydrolysis; and exposure of hydrogels to enzymes that can break the polymer backbone of the hydrogel matrix (Meyvis et al. (2000)). Research had been conducted to evaluate the effect of degradation on the swelling of hydrogel. The swelling is affected by the mechanism of degradation. In the former case where the crosslinks are degraded, the density of crosslinks in the matrix reduces resulting in an increased swelling until a stage where the hydrogel becomes unstable. In the latter case of enzymatic degradation of polymer backbone, the crosslinks remain with no loss of crosslinking density in the hydrogel matrix, resulting with no changes in swelling until it drops after the matrix destabilizes (Meyvis et al. (2000)). In view of application in agricultural lands, as seen in section 4.2, the hydrogels in soil serve as sources of carbon and medium for locomotion for microbes in the soil. The microbes feed on the substances that the hydrogel is made of as well as the compounds released after the collapse or degradation of the hydrogel matrix. Thus, biodegradation is a possible option and arguably the most coveted degradation mechanism for hydrogels. Chitosan was the first explored material with respect to biodegradability in hydrogels since it had better mimic of cell behavior. Chitosan is N-deacetylated chitin which is found in various bacteria, fungi, and crustaceans

(Qureshi & Khatoon (2015)). Qureshi & Khatoon (2015) conducted a 12-week open environment degradability test of chitosan-based hydrogel with soil. It proved the biodegradability of the same.

Biodegradability is a sought-out property for hydrogel to be applied in agriculture and could be a sustainable mechanism. Several studies have been done to assess variety of hydrogels for biodegradability. Natural polymer-based hydrogels degrade easily in soil, while synthetic polymers take very long to degrade as detailed in section 2.1 (Jamnongkan & Kaewpirom (2010)). Over the past few decades, the preparation of super absorbents has been primarily based on synthetic polymers such as acrylic acid (AA) or acrylamide (AM), which could be potential environment hazards due to their poor biodegradability (about 10% per year) (Cannazza et al. (2014), Zhang et al. (2014)).

In section 4.2, the products of pyrolysis of polyacrylate based hydrogels have been mentioned. The compounds of degradation from biodegradation as well as pyrolysis were similar with varying fractions of hydrocarbons and fatty acids. Some products of pyrolysis were unique such as long chain amides, esters, silanes, and sulfonyl groups (Rudzinski et al. (2002)) which pose toxicity to the biota and environment. It is argued that while polyacrylates are nontoxic, only the monomer acrylamide is toxic. The degradation products of this polyacrylate cellulose based hydrogel are said to be carbon dioxide and amines only and could be identified by use of carbon 13 isotopes (Wilske et al. (2014)). The C=O group was labelled with carbon 13 isotope for every 5 crosslinks. The amount of carbon 13 detected in the carbon dioxide emitted from the soil hydrogel sample at regular intervals showed that the overall degradation was less than 1% in 6 months (Wilske et al. (2014)). A study done by Stahl et al. (2000) explored the biodegradability of polyacrylate and polyacrylamide copolymer with white rot fungus in soil along with soil microbiome. The study showed that the microbial degradation was very low when compared to fungal or fungus-microbe coupled degradation. However, degradation was sufficient to validate. In an open environment degradation study, it was unequivocally presented that the degradation of the polymer-based hydrogel occurred due to microbial action.

Studies also verified the change in swelling properties of the hydrogel over a period of time. Fourier transform infrared spectroscopy, differential scanning calorimetry, thermogravimetric analysis, x-ray diffraction, and field emission scanning electron microscopy were conducted to gain insight into the microscopic structural changes (Qureshi & Khatoon (2015), Meyvis et al. (2000)). These provide data on the development of structural characteristics, which can be reviewed to examine the deterioration of the gel backbone. Porosity, shape and surface variations were reviewed using scanning electron microscope in the studies. Freezing and drying process was used to preserve the morphology of the Gel section (Montesano et al. (2015)). Small depositions were detected, which were construed as microorganisms after decomposition of the substrate. It was observed that the hydrogel using nutrients for microbial growth had helped in rapid decomposition (Qureshi & Khatoon (2015)).

Several commercially available hydrogels are based on polyacrylates with few alterations to the polymer backbone with cellulose (Kalhapure et al. (2016)). The insufficiency and contradicting results arise from studies done from different approaches. There is a need for establishing an integrated approach towards testing degradability by microbes, and identification of residual degradation compounds from pyrolysis and microbial degradation. The integration would help in determination of short term and long-term toxicity or nontoxicity of hydrogels. This problem could be eliminated by a shift towards using natural polymers completely replacing synthetic polymers which require special enzymes for effective decomposition. It could be favourable for sustainable agriculture practices.

The degradation products and the monomers extracted from AM-SHMB (tulipalin-A based hydrogel) showed no cytotoxicity on fibroblast cells (Kollar et al. (2016)). Cellulose based hydrogel degrades easier in sandy soils under the action of soil microbiome enhanced with nutrient release (Nie et al. (2004)). A study done by Ekebafe et al. (2011) investigated the process of degradation of gum tragacanth-acrylic acid-based hydrogel by soil microbiome and observed a 92% degradation in 10 weeks. The study found that the degradation products enhanced the carbon content, phosphorus and potassium contents of the soil which promotes plant growth. A slight decrease in pH of about 1.5% (within limits) was observed. A similar study by Saruchi et al. (2016) showed significant increase in plant nutrients availability in soil with a 3% increase in pH. The variability is a result of soil properties and existing conditions. Since the variability is within limits, it can be neglected. The breaking down of several polymers into respective monomers with the release of nutrients in the soil increases nutrient efficiency and availability of the soil.

Conclusion

Agricultural sustainability is essential to enhance food and water security, particularly in the context of climate change. In the recent past application of hydrogels in agriculture have received substantial attention among researchers as well as among farmers. Like its medical applications, a wider scope for hydrogels has been identified in agriculture. Hydrogel could be envisaged as an effective soil conditioner in arid and semi-arid regions. It would enhance soil texture; provide the required porosity for optimum flow of air and water; mitigates the effect of soil salinity on plants; and release of stored water in dried soil. As the typology of materials is of importance for research and development, the study makes an attempt to present various hydrogel classifications. Ideal properties to be considered for synthesis of hydrogel agricultural application have been identified. There exists a tradeoff between natural and synthetic polymers for their degradability and durability. Comparative studies on the growth of plants have been proven to be extremely valuable. Hydrogels are good soil conditioners which can improve water use efficiency, plant health and yield, and can reduce irrigation water requirements. Hence hydrogel application would be beneficial for crops such as paddy and wheat which have large water footprints.

Further studies could definitely be conducted on developing hydrogels which can mitigate the effect of saline soils on the crop growth. Novel stimuli-responsive hydrogels with release mechanisms based on moisture and time, for efficient use of fertilizers, pesticides, and fungicides. Natural polymer-based hydrogels should be studied in detail in view of improving biodegradability and water retention capacity. Such an understanding would help nations such as India for increasing the irrigation efficiency and soil conditioning for sustainable agricultural production. Further studies on the laboratory test methods on the hydrogel durability is found to be necessary to make it affordable for the farming communities and for its cost-effectiveness while scaling up to the farm level. Discussions on hydrogel properties and degradation show that there is a need to develop an integrated framework for test methods of various properties, for effective comparison of results for agricultural use. With adequate further studies we foresee the popularity of hydrogels among the farming communities for various crops. Integrating innovative solutions with environmentally-friendly hydrogels in the coming decade will contribute to the pursuit of achieving sustainable development goals.

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