Eco-friendly Three-dimensional Hydrogels for Sustainable Agricultural Applications: Current and Future Scenarios

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Abstract

Modern world is searching for water efficient agriculture techniques as irrigation is becoming scarce. Limited water resources and more food demand are the two key challenges in agriculture. Hydrogels which can respond intelligently by pH, temperature, light, ionic strength, osmotic pressure, magnetic or electric field changes are termed as intelligent or smart hydrogels which are analogous to conventional hydrogels in preparatory methods and features. Lag phase, constant release and decay phase are three steps involved in release of nutrients from polymeric hydrogels. In fact, hydrogels act as little reservoirs of water and dissolve nutrients that are released in controlled manner anchored by plant roots via capillary action. Hydrogels also sustain optimum amount of water in water stress conditions and reabsorb water in moist conditions which ultimately increases seedling, seed germination, plant growth and crop yield. Fertilizer and salt release are majorly dependent upon pH and temperature followed by diffusion-controlled mechanism. Cross-linkers, binders and fillers play pivotal role in determining properties, architecture and hydrogel pores. In comparison to potassium (K^{+}) and phosphate (PO_4^{-3}) ions, nitrates (NO_3^{-1}) and ammonium (NH_4^{+1}) ions exhibited faster release rate. This review spotlights application prospects of three dimensional hydrogel in agriculture. Initially, properties of hydrogels, their classification, preparatory methods, effect of natural-synthetic-polymer blending and role of fillers are stated. Afterward, hydrogel functioning, significance, advantages, mechanism of fertilizer release and agriculture specific applications of hydrogels are comprehensively described. In conclusion, extraordinary biocompatible, cheaper, stable, biodegradable, durable, non-toxic and re-wettable characteristics of hydrogel systems motivated their utilization in agronomical applications.

KEYWORDS: 3D-Hydrogels, biopolymeric blending, nanofillers, agricultural applications, control release fertilizers

1 INTRODUCTION

Agriculture is the foremost consumer of water. Now days, agriculture is under strains of drought, temperature and salinity that is expected to rise due to climate change, urbanization, overpopulation and land degradation. Irrigation of plants to cope water stress is a limiting aspect that influence productivity, crop yield and fruit development.[1] Modern world is searching for water efficient agriculture techniques as water irrigation is becoming scarce. Decrease in water resources and more food demand are two key challenges in agriculture sector.[2] Therefore, it is imperative to adopt management approaches to uplift water holding capacity of soil and improve crop yield. The finest way out to overcome aforesaid challenges are hydrogels. Hydrogels are three-dimensional (3D) cross-linked hydrophilic frameworks which absorb large quantity of water without dissolving in it. In addition, soft, smart and water storing capabilities of the hydrogels make them unique contenders for agricultural applications.[3] Similarly, hydrogels are polyelectrolytic polymers which are superabsorbent, permeable and transparent that increase water availability, holding capacity and irrigation potency for plants.

1.1 Hydrogels

Hydrogels are 3D frameworks comprised of hydrophilic polymers which are cross-linked by intra/inter-molecular forces. These can be prepared in diverse sizes and forms that are capable to captivate water without dissolving in it. Hydrogel have significant importance in agricultural sector for applications as soil conditioner, nutrient carrier and sustained fertilizer release.[4] The swelling action is a distinctive behavior of hydrogels in water, ionic, buffer and saline solutions. This swelling is governed by pH, temperature, polymeric nature and cross-linking that enable to use them not only in agriculture but also in biology, industry, cosmetics and bio-sensing appliances.

1.2 Background

Hydrogel agriculture technology encompassed gel making hydrophilic polymers which absorb water without dissolving in it. Agricultural hydrogel was reported in 1980s for improvement in efficient use of water and modification of physical properties of soil. The Indian agriculture research institute (IARA) fabricated a new hydrogel (branded as Pusa hydrogel) and explored for agronomic use to overcome drought and to ensure efficient water use in some semi-arid and arid regions of India.[5] Initially, sodium and potassium polyacrylate were explored for development of agriculture hydrogel due to their superabsorbent and water insoluble nature.[6] Preparation of hydrogels from natural polymer is currently the focus of modern research in hydrogel agriculture.[7]

1.3 Swelling Ability

The swelling action is unique property of hydrogels which is different in water, pH and ionic strengths that enabled their use in agriculture, biology, industry and medical field.[8] Covalent interactions, secondary forces and chain expansion are liable for swelling in hydrogels.[9] Water diffusion, loosening of polymeric networks and swelling are three main steps involved in hydrogel swelling. Dehydrated state in hydrogel is known as glassy form and swollen state is regarded as rubbery form. When water infiltrates into hydrogel network, it causes relaxation of polymeric chains followed by enlargement and ultimately transforms glassy form into rubbery form. Diffusion is the process responsible for entrance and exit of water from hydrogels. The swelling sequence is depicted in Figure 1.

The percentage increase in swelling was calculated by Equation (1):

$$Swelling\ (g/g) = \frac{W_S - W_d}{W_d} \quad (1)$$

Whereas, dry weight is denoted as "W_d" and "W_s" stands for swelled weight of hydrogel.

The porosity of soil is also altered by the swelling action of hydrogels. The influence of swelling on porosity changes in soil is illustrated in Figure 2.

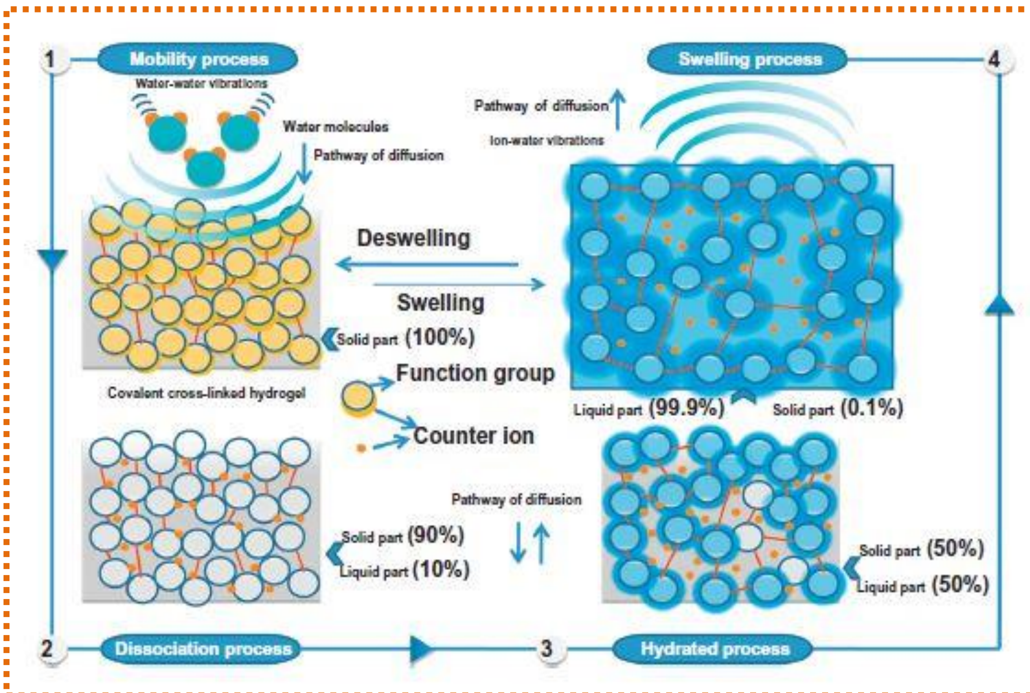

Figure 1 The order swelling in hydrogel adopted with permission from Ghobashy et al.[7]

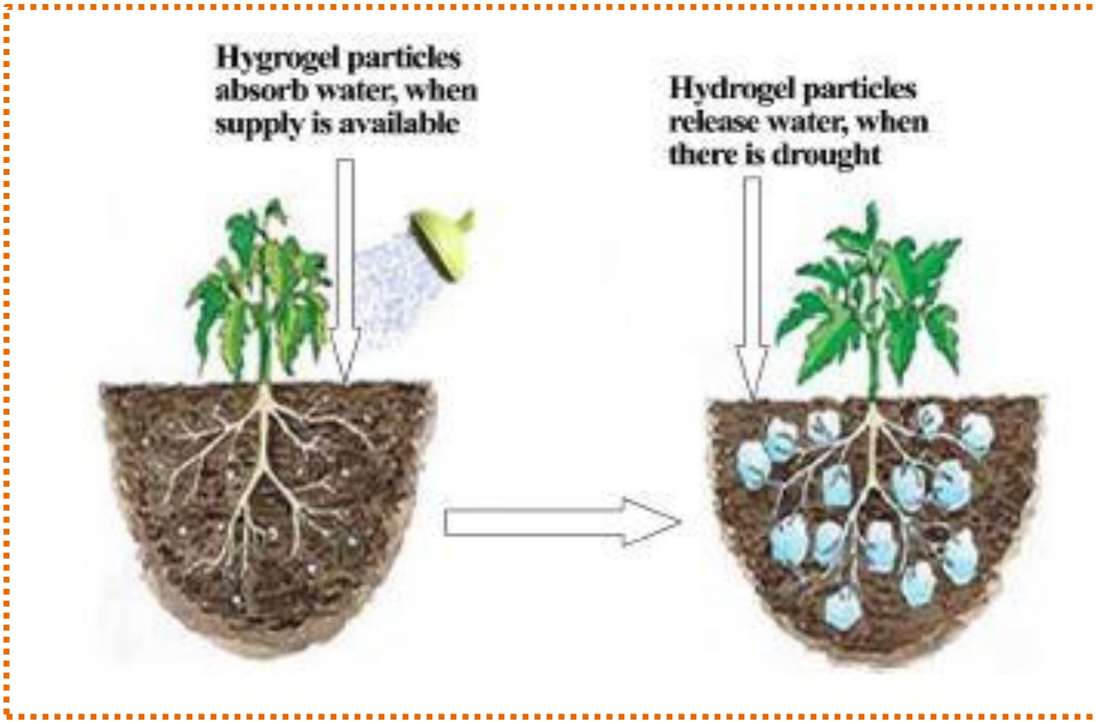

Figure 2 The impact of hydrogel on porosity of soil adopted with permission from Kabir et al.[10]

1.4 Classification of hydrogels

Hydrogels are classified on the basis of origin, charge, cross-linking, shape and response. Natural, synthetic and semi-synthetic hydrogels are three main categories of hydrogels established on the basis of their origin.[11] Hydrogels comprised of secondary or non-covalent interactions among polymeric chains are stated as physical hydrogels. In chemical cross-linking covalent interactions are developed between two unlike hydrophilic polymer.[12] Charge is another benchmark that classifies hydrogels into cationic, anionic and zwitterionic hydrogels.[13] Hydrogels bearing charges are generally pH sensitive. Hydrogels incorporated with cationic polymers like chitosan ionized only at pH values less than 7 and vice versa.[14]

Hydrogels which respond by various stimuli and their properties can be altered by some external factors are regarded as intelligent or smart hydrogels. These are analogous to conventional hydrogels in features and preparatory methods but show intelligent responses to pH, temperature, light, ionic strength, magnetic or electric field.[15] Smart pH sensitive hydrogels consists of ionic pendant groups distributed along their backbones such as poly (diethyl-aminoethyl methacrylate) (PDEsAEMA), poly (methacrylic acid) (PMAA) and poly (acrylic acid) (PAA). These hydrogel presented different swelling volumes at different pH which could be tailored for their utility in agriculture. Thermo-responsive hydrogels use temperature variations for their gelation behavior deprived of external stimulus.[16] Several hydrogels coagulate above certain temperatures. Many biopolymers like chitosan, carrageenan, gelatin cellulose and dextran derivatives undergo gelation by changing temperature.[17]

1.5 Hydrogel properties

The properties of hydrogels are reliant on polymers and their pendant functional groups. Hydrogels are hydrophilic, high swelling, flexible, easily shapeable, porous, soft and elastic in nature.[18] These respond intelligently upon temperature, light, ionic strength, pH, osmotic pressure, magnetic and electric field fluctuations. Biocompatibility, non-toxicity, stability and biodegradability are major characteristics of hydrogel materials. The physico-chemical characteristics of hydrogels are considerably enhanced by cross-linking and integration of filers or reinforcement materials.[19] In physical cross-linking microenvironment controls are inadequate because it is reliant upon the intrinsic properties of the polymer. On other hand chemical cross-linking processes are precise for development of 3D hydrogel frameworks.[20]

1.6 Hydrogel preparation

Hydrogels can be developed by various techniques such as copolymerization of hydrophilic monomers with functional groups such as $-NH_2$, -COOH, -OH and -C=C- using cross-linkers. In case of unsaturated double bonds monomer initiator is essential to initiate polymerization. Poly-functional cross-linkers are engaged in solution polymerization.[21] Following are some methods opted for hydrogel preparation:

- Free radical polymerization
- Co-polymerization method
- Chemical cross-linking
- Physical cross-linking
- Poly electrolyte complexation
- Solution casting method

Being cost effective, biocompatible and biodegradable mostly natural polymers are employed for hydrogel synthesis.

1.7 Biopolymers

Biopolymers could be the ideal customers to increase water retention capacity of soil due to their biocompatibility, non-toxicity, abundance and degradability in the soil by microbes in ambient environments.[22] Depending upon chemical structures biopolymers are classified as polymeric proteins, polysaccharides polyamides, polyphenols, nucleic acids and poly-isoprenoids etc.[23] There are five different methods by which biopolymers are transformed into hydrogel that include inverse, internal, interfacial, external and multistep gelation.[24] Among natural polymers, polysaccharides are widely employed in agronomic hydrogel applications that comprised of sugar units bonded with 1-4 glycosidic linkage which have general formula $(C_6H_{10}O_5)_n$. Chitosan, carrageenan, glycogen alginate, cellulose, starch, guar gum and agarose are commonly employed polysaccharides in hydrogel preparation.[7]

1.7.1 Polysaccharide-based hydrogels

Polysaccharides exist as biopolymers that have massive variety in their structures and bio-functionalities. These can be regarded as renewable biomaterials owing to their safety and ease of modification.[25] Primarily, polysaccharides are acquired from various origins like plants (starch, pectin, psyllium, guar gum, cellulose, hemicellulose, locust bean gum, gum acacia and agar), Microbes (xanthan, curdlan, levan and gellan), algae (alginate and carrageenan) [26] and marine organisms (pullulan, scleroglucan, chitin, chitosan and hyaluronic acid).[27] Figure 3 illustrates sources and applications of some polysaccharides. Polysaccharides are expansively considered for variety of agricultural, biomedical, industrial and pharmaceutical applications. Their utility already have been recognized as thickeners, stabilizers, geller, film-formers, emulsifiers, lubricants, and fertilizer carriers.[28] Natural polysaccharides are categorized as soluble and insoluble however; water soluble polysaccharides are preferred as soil conditioners and avert soil crusting. These also improve efficiency and sustained release of fertilizers.[29] In contrast to non-biodegradable hydrogels, polysaccharide based hydrogels are preferred for agricultural applications owing to their biodegradable nature. Among polysaccharides, chitosan elicit and boost defense system of plants.[30] It is also reported that bean treatment along with chitosan inhibited necrosis caused by mosaic virus.[31] Some natural polysaccharides are shown in Figure 4 which are commonly employed for hydrogel preparation.[32]

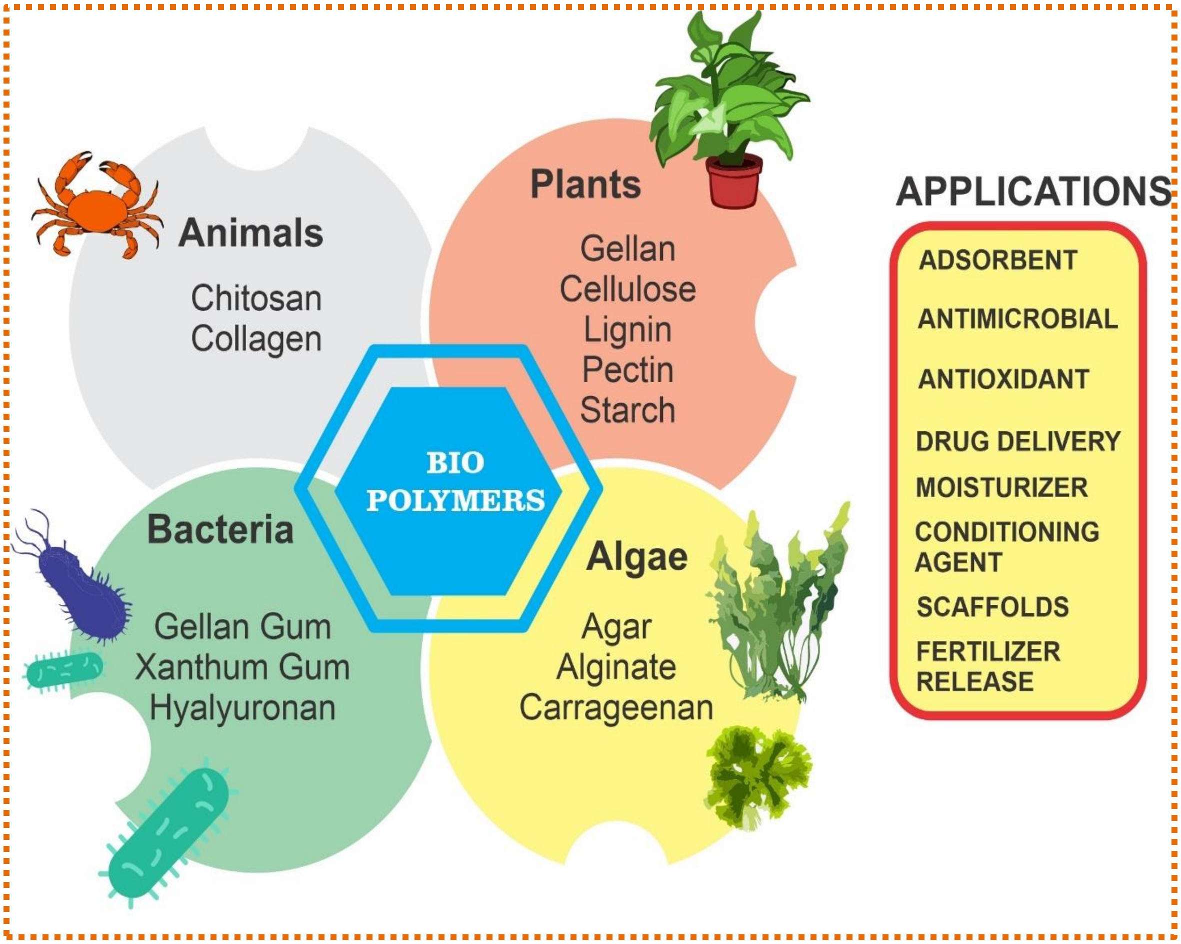

Figure 3 Hydrogels obtained from natural sources and their applications adopted with permission from Bahú et al.[33]

The polysaccharides alone are unable to produce cross-linked hydrogel with higher stabilities which is the prime requisite for soil conditioners and fertilizers release applications.

1.8 Natural-synthetic hydrogel blends

Synthetic polymers have demonstrated biocompatible, water absorbing and flexible features similar to the biopolymers so, they are blended with nature polymers to obtain hydrogels with much improved mechanical strengths. Natural-synthetic polymeric blending has been carried out for resistance and resilience to degradation upon copolymerization. Synthetic polymer which is rich in oxygen permeability is useful in formation of agronomic hydrogels that not only promote aerobes in the soil by nitrogen fixation but also assists in availability of nutrients.[34]

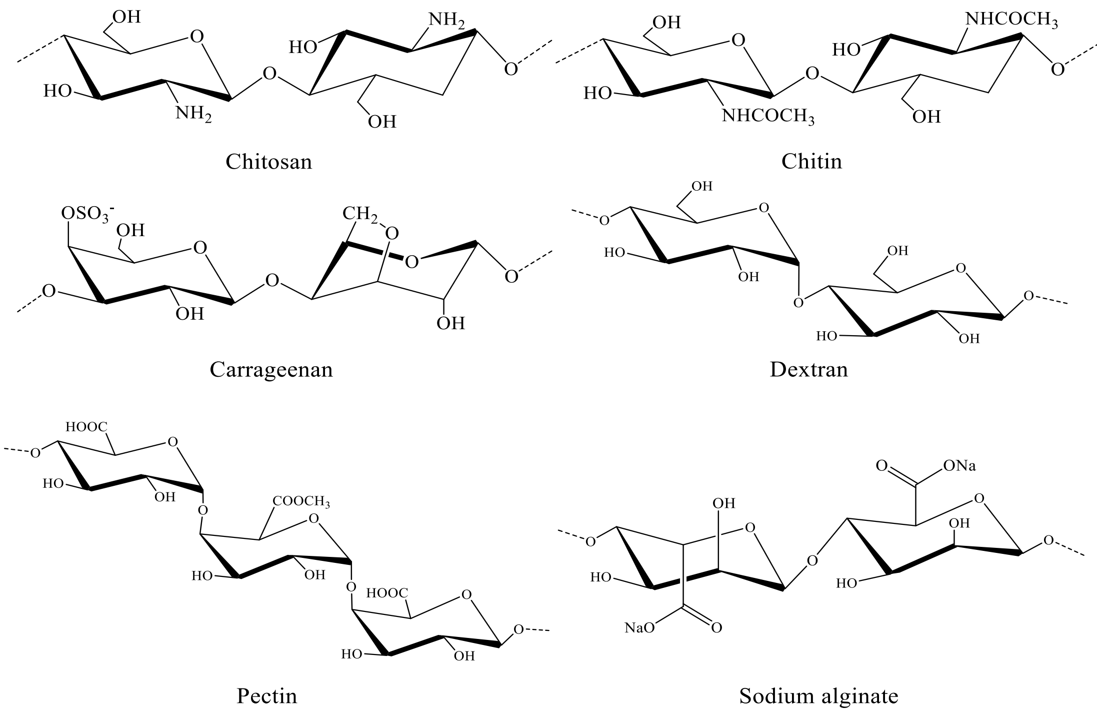

Figure 4 Chemical structure of some biopolymers used in hydrogel synthesis.

Fabrication of hydrogels that possess time period prior to the degradation is achieved by the assistance provided by synthetic polymer. A synthetic polymer increases polysaccharide gelation in aqueous medium, sustains fertilizer release, enhances binding affinities of ions in the soil, increases thermo-stability and resist against chemicals and ultraviolet radiations. There are numerous synthetic polymers which are commonly explored for development of agriculture hydrogel. For instance, poly vinyl alcohol (PVA) was integrated with chitosan for preparation of hydrogel beads for agriculture applications. The main advantage of PVA is its ability to form inter and intra molecular hydrogen bonding with chitosan.[35] Recently, a novel PVA/ poly (N-vinylpyrrolidone) (PVP) hydrogel was reported by Malka et al for entrapment and release of hydrogen peroide.[36] Polyurethane (PU) hydrogels were also prepared by varying molar mass of poly (ethylene glycol) (PEG) and investigated their effect on tomato growth. Authors concluded that hydrogels promoted tomato growth due to the improvement in water retaining efficiency.[37]

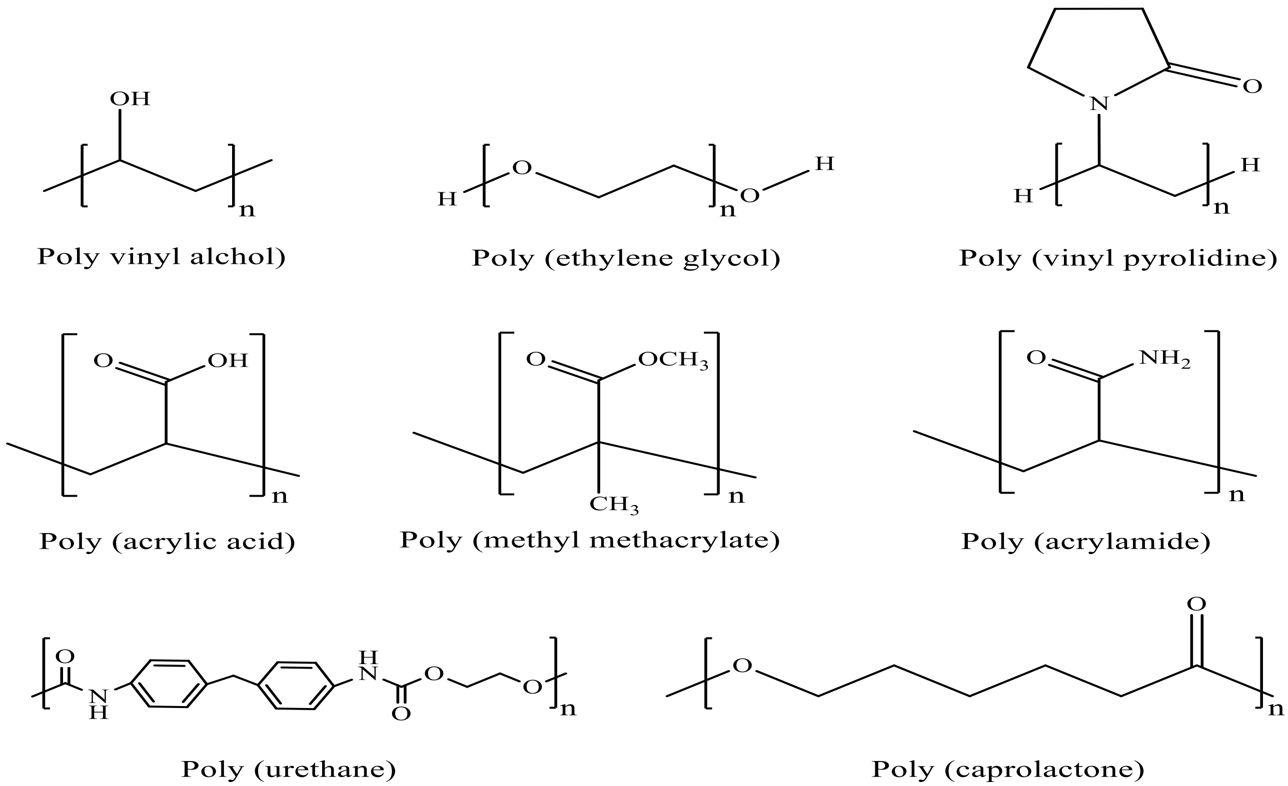

Figure 5 Some synthetic polymers employed in hydrogel development for agriculture.

Table 1 Hydrogels derived from natural-synthetic polymer blending adopted from Venkatachalam et al.[38]

Sr. No	Characteristic hydrogel	Reference
1	Starch-modified PAA	39
2	Natural cashew tree gum and PAM	40
3	Wheat straw cellulose established hydrogel	41

4	Hyaluronate-hydroxyethyl acrylate blend	[42]
5	Guar gum-g-poly(sodium acrylate) hydrogel	[43]
6	Gum ghatti-PAA–aniline	[44]
7	Chitosan-PAA	[45]
8	Carrageenan-PVP	[46]
9	Carboxymethyl cellulose (CMC)/ N-vinyl caprolactam	[47]
10	Chitosan/CMC/PVA	[48]

Karadağ et al. reported poly (acrylamide) (PAM) and crotonic acid hydrogels incorporateg for release of sulphate, nitrate and ammnium fertilizers. This research group also studied successful loading and release of agriculture drug sodium 2,2-dichloropropionate (also known as Dalapon).[49] The retention of a fertilizer is also an important factor for agricultural utilization of hydrogels. Wu et al. coated cellulose acetate superabsorbent hydrogels with PAA and PAM which revealed superior water retentive and fertilizer encapsulation/release abilities.[50] Poly(hydroxybutyrate)(PHB) based composites were also reported for release of nitrogen, phosphorous and potassium fertilizer.[51] Chitosan were also grafted with PMMA as urea carrier. Authors also studied adsorption and desorption of urea for agronomic applications.[52] Poly caprolactone (PCL), polyether polyol (PEP) and PU were also reported for fabrication of agriculture hydrogels.[53] Chemical structures of synthetic polymers used in hydrogel fabrication are provided in Figure 5**.** Some hydrogels fabricated by natural-synthetic polymer combinations are depicted in Table 1.

1.9 Nanofillers (NFs)

Mechanical properties of polymer matrix are upgraded by integration of nanofiller (NF) that produces new materials which are receptive to biological, physical or chemical stimuli. Several types of NFs have been combined with diverse types of polymers to accomplish anticipated characteristics in hydrogel frameworks dependent on type of applications.[54] NFs are categorized as follows;

1.9.1 Organic and inorganic NFs

Organic NFs include polymers, natural clays, nanofibers and natural fibers. Natural fibers includes cellulose, flax and wood etc.[55] Inorganic NFs comprise of nanoclays, metal oxides such as Cu_2O, MgO and Fe_2O_3. Amongst metal particles gold, silver and iron are usually used. Nanoparticles (NPs) of CdS, PbS and MoS_2 are also incorporated as inorganic fillers.[56]

1.9.2 Inert and active NFs

NFs which can only improve mechanical properties of hydrogels but do not divulge stimuli-responsive features are known as inert NFs. Silica, cellulose, and clay-based NPs are frequently used as inert NFs.[57] Graphene based NFs that impart stimuli-response aptitude to hydrogel together with mechanical improvements are termed as active NFs.[58]

Hydrogel showcased their significance as root watering crystals and water retentive granules.[59] At present, hydrogels face some challenges in bearing load, mechanical performances and fertilizer loading/release abilities. For rapid commercialization of hydrogel agriculture technology it highly needed to address aforementioned limitations. As for as future prospect is concerned, hydrogel agriculture technology is boon for sustainable agronomy in drought, urban forming, cultivation in sandy soils, improving crop yield, sustained release of fertilizers, seed germination inside hydrogel.[60]

2 HYDROGELS IN AGRICULTURE

2.1 Significance of hydrogel in agriculture

Hydrogels displayed smart features such as stability, nutrient reservoir, biodegradability, non-toxicity and swelling/deswelling characteristics which empowered their utilization in agriculture. For example, hydrogels have demonstrated optimized and higher absorption capabilities in hard and saline water conditions. These are durable, photo-stable, cheaper and re-wettable which produce less soluble contents without creation of toxic substances. Hydrogels exhibit water imbibition characteristics which enabled hydrogel to alleviate certain concerns in agriculture. Hydrogels not only effect soil density, permeability, texture, structure, humidity and water penetration from soil but also decreases irrigation frequencies. Soil compactness, erosions and water runoff and microbial actions were also reduced by hydrogels.[61] Super-absorbing hydrogels act as minute water reservoirs through which water is absorbed by the plant roots due to osmotic pressure gradient. Water holding ability of sandy soil is significantly enhanced as well.[62] The hydrogels played pivotal role for slower and sustained release of nutrients and fertilizers by holding them which were absorbed by the plants. Plant roots anchor the water and dissolved nutrients according to their needs and improved plant growth and development.[63] Researchers have reported that adding hydrogels 2g/Kg raised water holding capacities of sandy soils from 171% to 402%.[64] Thus, hydrogel applications minimize irrigation requirements. Apart from aforesaid advantages hydrogels exhibited maximum absorbency even at higher temperatures, stability in soil and inferior rates of application in crops 2.5-5 kg/hectare (ha). These also decreases leaching of herbicides, support plant in water stress and enhances physical properties of soil. Seedling, seed germination, root growth, flowering and fruiting are also enhanced by hydrogels in agronomy.[65]

2.2 Hydrogel functioning in water retention and release behavior

In hydrogels, intrinsic functionalities present in polymeric chains are accountable for absorption of water. When water interacts with polymeric network inside hydrogel, water is absorbed by diffusion and hydrogen atoms react and produce positive ions. As a result, numerous anions are formed over the entire length of polymeric chains which repel each other that unwinds and opens polymeric frameworks. Water is attracted by the polymers thru hydrogen bonding and hydrogel absorb water 400-1500 times of their dry weight. This absorbed water act as a water reservoir. When root hairs starts to dry 95 % of stored water is provided by the hydrogel reservoir.[66] Under moist environment, again hydrogel rehydrates and achieve water restoration so; polymer recovers water availability and increases crop growth. The whole phenomenon of hydrogel interactions in soil is explained by Figure 6.

The volume changes displayed by the hydrogels are dependent on fundamental environmental conditions.[67] Hydrogels are advantageous in sense that do not affect physicochemical characteristics of soil as these are biodegradable and decomposed with the passage of time.

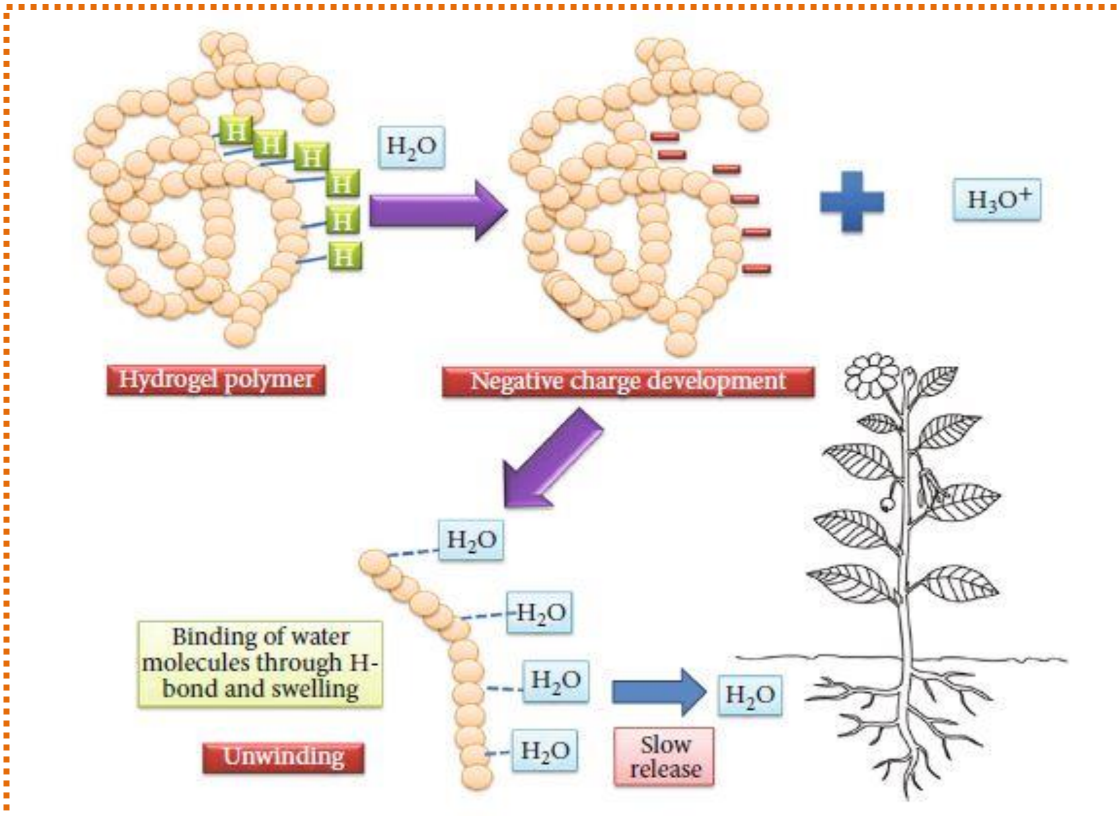

Figure 6 Hydrogel mechanism of action in soil applications adopted with permission from Patra et al.[59]

2.3 Fertilizer release mechanism

There are three steps for the release of nutrients from polymeric hydrogels are lag phase, constant release and decay phase.[68] In the first step water present in soil penetrates into polymeric networks from the cracks or pores present in hydrogel. The cracks and pores become wet and very small portion of fertilizer such as urea is dissolved. At this stage, fertilizer release does not take place while vapor pressure is the driving force which governs swelling in hydrogel. This stage is known as lag phase as time is required to fill inner spaces to accomplish steady state between flux of water and leaving fertilizer.[69] In the second step, water continuously infiltrates and dissolves fertilizer that uplift osmotic pressure inside hydrogel followed by the accumulation of critical water volume which allow fertilizer release among cracks and pores. As concentration of fertilizer inside is saturated, therefore, diffusion of fertilizer in the soil is constant known as constant release.[70] In decay phase, pressure surpasses recommended threshold which ultimately rupture the hydrogel network and instantly releases fertilizer. In this stage, maximum content of fertilizer has been released that decreases concentration gradient and driving force.[70] Figure 7 explains all steps involved in controlled release of fertilizers. The mechanism of release is complex, sigmoidal (S-shape) and non-linear. The researchers aim to achieve sigmoidal release profile for fertilizer release by fabrication of various formulations to obtain controlled release matching nutrient requirements of plant.

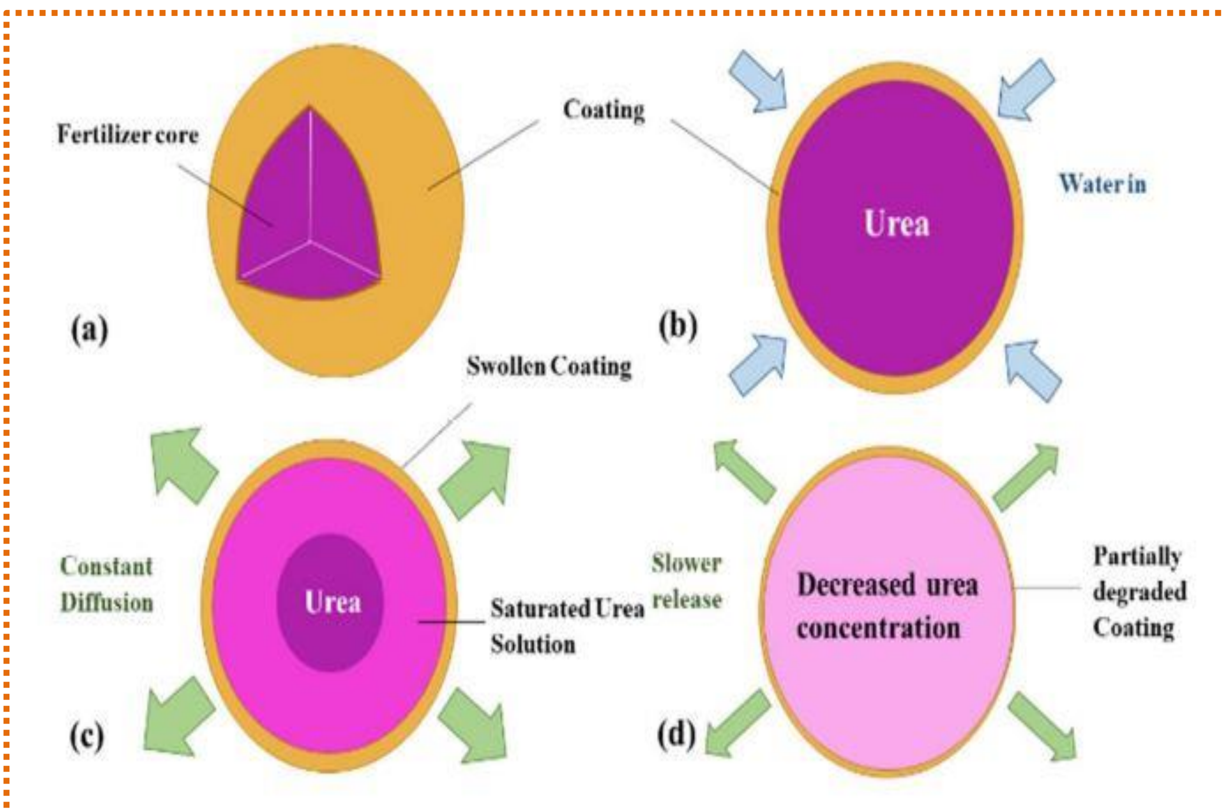

Figure 7 Mechanism of controlled release. (**a**) Controlled release granule. (**b**) Lag period (**c**) Constant. (**d**) Decay stage. Adopted with permission from Lawrencia et al.[71]

2.4 Factors affecting fertilizer release

The release rate of fertilizer is generally affected by size, coating thickness, selection of polymeric materials, filler and cross-linker. For hydrogels pH, temperature, and ionic strength also influence the release rate.

2.4.1 pH

Among hydrogels, pH is vital aspects that influence swelling volumes which eventually affects discharge of integrated fertilizers.[72] The pH of soil straightly affects the nutrient availability. As some fertilizers are insoluble at low or high pH which limit absorption of fertilizers for root hairs. Henceforth, pH-sensitive behaviors from hydrogel avert additional fertilizer release which has promising applications in horticulture, nurseries and agriculture. The acidic and basic nature of soil determines nature of interactions, diffusion coefficient of ions and fertilizer.[73] In acidic conditions (pH 2-5), H^+ ions are in excess that protonate the anionic groups thus diminish anion-anion repulsions and decreases swelling capabilities. In basic media, above pH 9, cations such as Na^+ shield the carboxylate and other anion which also reduce anion-anion repulsive forces and swelling action decreases. Swelling capabilities are probably highest due to the conversion of COOH groups into carboxylate moieties at pH 5-9 range due to buildup of stronger anion-anion electrostatic repulsion.[74] However, there are certain studies reported which illustrated hydrogel swelling at pH 2 and 10 as well.[75]

2.4.2 Temperature

Thermo-sensitive polymeric hydrogels are enticing field of research in past thirty years due to their performance, biocompatibility, cost-affectivity and flexibility.[76] The temperature increase is inversely related to lag period.[77] Temperature enhances nutrient solubility, porosity, diffusion, diffusion coefficients and release rates.[78] Bi et al. stated that increase in temperature by 15 ºC doubled the release rates. The temperature also stimulated hydrogel degradation in enzymatic environment.[79] Feng et al. developed smart pH and thermo-sensitive polymeric hydrogel by radical polymerization for controlled release of ammonium zinc phosphate fertilizer. The fabricated system not only improved supply of nutrients but also prevented excessive release of stated fertilizer.[80]

2.4.3 Ionic strength

In contrast to distilled water, the swelling volumes of hydrogels are smaller in ionic solution of NaCl, KCl, $CaCl_2$ and $FeCl_3$which can be explained by the decrease in osmotic pressure by the increase in charge/mass ratio. Salt cations screen the anionic groups like carboxylate ions with in hydrogel and reduce repulsive forces and decrease swelling in $Na^+ > K^+ > Ca^{+2} > Fe^{+3}$ pattern.[81] The increase in concentration of multivalent ions also produce complexes that increases number of cross-link points which hinder expansion in hydrogel and reduces release of fertilizer from hydrogel.

2.4.4 Granule radius

It is stated that fertilizer release can be regulated by the coating thickness and granule sizes. The lag stage is directly related to the radius of granules and coating thickness. The release rates and decay stage are inversely proportional to the lag stage. For controlled and slow release of fertilizer lag phase is extended by modulating granule sizes and coating thickness. By increase in radius of granules prolonged the lag phase which eventually releases fertilizer in slow and steady manner. In this way nutrients are appropriately supplied to the root hairs.[71]

2.5 Impact of granule size on plant performance

Agriculture hydrogels act as water retentive granules that swell up to innumerable cycles in contact to aqueous solutions.[82] These absorb moisture in water excess conditions while sustain plant roots in water stress environments.[59] These hydrogel granules are significant in soil-water retention and carriers for fertilizers, pesticides, insecticides and herbicides.[83] The mechanical properties which effect fertilizer carrying granular hydrogels are particle size, radius shape, density and flow ability.[84] Granule size is directly proportional to the lag phase which has inverse relation to the slow release of fertilizers. Henceforth, It is important to increase the granule size at optimal level which extends lag phase and slow release of loaded fertilizer.[84] Shaviv et al. also developed the models to determine the stages the fertilizer release mechanism.[85]

2.6 Methods to apply hydrogel in agriculture

Hydrogels act as a soil conditioner improve structure of soil, promote water retention and stabilize surface. For a sandy soil 5 kg/ha at 4 inches depth are used while in clay soil 2.5 kg/ha hydrogels are incorporated at 6-8 inches soil depth.[59] Dry and wet are methods used for application of hydrogels in soil. In dry method, specific quantity of polymeric hydrogels is applied to the subsoil at the deepness of 15-25 cm followed by moistening prior to crop cultivation. The swelled hydrogel improves soil structure, water penetration and retention. Wet method soil moistening was performed. The polymeric solution is sprayed followed by sowing the seeds instantly. Wet method minimizes water consumption and soil erosion.[59]

2.7 Advantages of agriculture hydrogels

Hydrogels have several advantages in agronomic sector. First of all, hydrogel are the mini water reservoirs which slowly releases water. This water is absorbed by plant roots by the mechanism of capillary action. Secondly, hydrogels sustain optimum amount of water by releasing water during water stress and absorb water in moist circumstances which ultimately increases seedling, seed germination and crop yield. Thirdly, at low temperatures water present in hydrogel frameworks do not freeze thus facilitates plant and prevent their death from freezing. Fourthly, osmotic moisture of soil is decreased, save irrigation, mitigate drought conditions, prevent leaching, restore soil organism and improve availability of water and nutrients to the plants. It is also helpful for plants as they can survive under severe water stress and postpone wilting. Fifthly, the hydrogel moderates the over usage of pesticides and fertilizers. Lastly, these inhibit soil compaction and enhance soil aeration and healthier plant growth was observed.[86]

2.8 Agriculture specific applications of hydrogels

Polysaccharides based hydrogels are pivotal in agriculture applications not only as carrier (fertilizer, nutrients and pesticides), soil conditioners and soil aerator but also provide optimum availability of nutrients, reduce toxicity, and minimize evaporation.[38] Figure 8 summarizes benefits of hydrogels in agriculture sector.

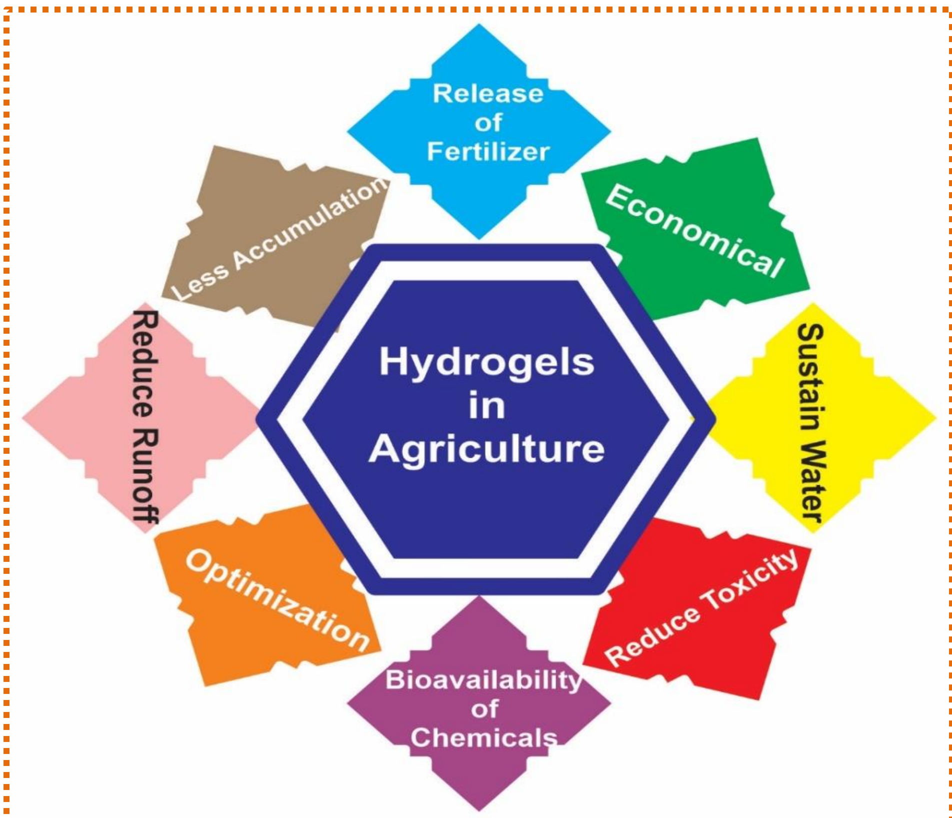

Figure 8 Advantages of hydrogels in agriculture sector.

2.8.1 Hydrogel beads for agricultural engineering

Owing to biological properties and structural diversity natural polymers such as chitosan, carrageenan agar, xanthan gum, sodium alginate, starch and guar gum are renowned entrants for the fabrication of hydrogel beads. For instance, chitosan-based NPs are promising candidates for effective delivery of agrochemicals (fertilizers, minerals, micronutrients, pesticides and herbicides). The advantage of biopolymeric materials is their affinity for many chemicals, low prices, selectivities and chemo-stability. Polymeric beads were also explored as a adsorbent in agro-engineering for removal of pesticides, herbicides, fungicides, phenols, dyes, metal ions and waste water treatments etc.[35]

2.8.2 Hydrogel enables nanofertilizers (NFz) release

Fertilizer loading in nano-structured form increase crop yield, seed germination, seedling, photosynthesis, nitrogen stability and carbohydrate contents.[87] Hydrogels were incorporated with diverse types of nano-materials like metal oxides, mesoporous silica, nanoclays and hydroxyapatite for carrying fertilizers. Fertilizers interact with these nano-materials and produce new NFz which are available for the plants.[88] The chitosan based NFz are employed in controlled fertilizer release.[89] These NFz are water soluble and encapsulated in NPs present in hydrogel framework which are released by diffusion into root hairs in sustained manner. This diffusion process followed apoplastic and symplastic pathway and entered into xylem tissues which are accountable for their transport to the various parts of plants including roots, leaves and stem.[90] Table 2 provides brief literature regarding hydrogels utility in controlled release of various fertilizers. The NPs size is very crucial for their entrance in the pores present in plant cell wall. The NPs with smaller diameter than pores of cell wall could easily cross the cell wall and reach to the cell membranes which eventually effects notable difference in seed germination.[91]

Table 2 Hydrogels designed for controlled release of fertilizers adopted from Venkatachalam et al.[38]

Sr. No	Characteristic hydrogel	Type of fertilizer	Reference
1	Microwave assisted biochar composite	Nitrogen fertilizer	44
2	CMC/PVP	Nitrogen fertilizer	92
3	CMC/PAA	Nitrogen fertilizer	93
4	Starch cross-linked PAA and PAM	Nitrogen fertilizer	94
5	Gelatin-Tapoica/PAM	Potassium fertilizer	95
6	Chitosan/PVA cross-linked with glutaraldehyde (GA)	Potassium fertilizer	96
7	MC/hydroxypropyl	Potassium fertilizer	97
8	Arabic gum	Potassium fertilizer	98
9	CMC hydrogel	Phosphate fertilizer	99
10	Alginate/cellulose nanofibers/PVA	Phosphate fertilizer	100
11	Alginate-graft-PAM	Phosphate fertilizer	101
13	Pectin $H^+/(NH_4)_2SO_4$	Ammonium fertilizer	102

Although, NFz stimulate plant growth but their use in smaller quantity is preferred to avoid health and environmental problems. Bortolin and his teammate's fabricated hydrogel made up of starch /PAM/calcic montmorillonite/methyl cellulose (MC) for urea carrier. It was observed that urea release was significantly regulated by the pH, hydrophilicity and hydrolysis. The outcome of the reported work indicated that 192 times slow release was illustrated by the reported hydrogel in comparison to pure urea. Further, 90 g of urea was released per gram of dried hydrogel.[103]

2.8.3 Agriculture hydrogel's impact on soil microorganisms

Microorganism such as bacteria and fungi are affected by physicochemical and biological atmosphere. These are responsible for decomposition of dead plant and animal residues and improve nutrient quantity in soil. Applications of hydrogels act as a minute reservoir of water-nutrients and release them in sustained manner. These water-nutrient reservoirs comprised of hydrogels are an excellent choice in agronomic purview not only to save water and nutrients but may also restore ecology. The impact of polymeric hydrogels on ecological restoration is not well understood due to slight available information. A group of researcher also stated that application of rice straw based hydrogel improved the growth of useful bacteria, fungi, phosphatase hydrogenase and actinomycetes in sandy and calcareous soils without any negative effect on plant nourishment.[104]

2.8.4 Hydrogels enables smart fertilizer release

Currently researchers are interested to develop sensing fertilizer which are slowly released by their encapsulation in smart hydrogels to overcome drawbacks of traditional fertilizers.[105] The efficacy of plant fertilizer is improved by their coating over smart biodegradable hydrogels which is recognized as polymer-coated fertilizers.[80] This strategy improves fertilizer performance by providing prolong access to plant roots, reduces compactness and increase crop yield. Fertilizer release can also be stimulated by external stimulus such as temperature, pH, biological activity and osmotic pressure.[106] Adam et al. investigated effect of temperature on release of micro and macro nutrients known as Polyon, Nutricote, and Osmocote. The author concluded that effect of temperature is more uniform on Nutricote relative to Polyon and Osmocote. The release of each fertilizer was postponed 20-40 days. In addition, fertilizer release was minimum in 5-15 ºC while steady state release were observed in 20-30 ºC temperature.[106] Inorganic salt release studies were conducted by Oertli et al. several elution experiments. The release of salty fertilizer was majorly dependent upon pH and obeyed diffusion mechanism. The increment in temperature from 10-20 ºC also directly influenced release rate. In comparison to potassium and phosphate ions, NO_3^{-1} and NH_4^{+1} exhibited faster release.[107] Research group of Meurer indicated successful release of iron from poly (allylamine) hydrochloride hydrogel for iron deficient cucumber plant. It was observed that chlorophyll content in cucumber leaves was increased, which confirmed efficient deliverance of iron ions from hydrogel.[108] Extensive researches are needed to develop quick, efficient and more effective smart biodegradable hydrogels for controlled release of inorganic fertilizers.

2.8.5 Improvement in fertilizer availability

Hydrogels can be prepared by incorporating fertilizer as their constituents with the aid of potassium and nitrate ions. Thus, chemical persist in hydrogel frameworks are released slowly and assimilated by the plant roots. For example, Konzen and his teammates prepared hydrogel which comprised of collective effect of nitrogen, phosphorus and potassium (NPK) superphosphate, potassium chloride as a component. The results indicated higher growth, seedlings, nutrient absorption and water holding capabilities.[109]

2.8.6 Soil modifications

Improvements in soil characteristics can be brought by the use of hydrophilic 3D cross-linked polymeric hydrogels. Apart from water-nutrient reservoirs hydrogels are also utilized for soil preservation, ameliorate undesirable dehydration and to cope moisture stress in crops.[110] The use of hydrogels in soil has many advantages. Water and nutrient carrying long-lasting hydrogels safeguard soils from runoff flow, promote fertilizer efficiency, improve performance and enhance microbial activity in the soil.[111] Barkat and coworkers stated drawbacks related to traditional irrigation technologies can be avoided by utilization of polymeric hydrogels which ensure water absorption and retention.[112]

2.8.7 Reduction in labor cost and higher crop yields

Sustained release fertilizers were explored to meet nutrient demands of crops, fruits and vegetables such as rice, strawberries, melon, banana, kiwi, pepper, onion and tomatoes.[113] Hydrogel coating supplied nitrogen to the rice fields effectively and delivered essential nutrients in sustained manner.[114] Cirrus forming also has significant potential for the employment of controlled fertilizer release technology.[115] These crops produced high yield, better quality and handsome income for farmers with minimum labor cost. Figure 9 portrayed urea release from a superabsorbent hydrogel.

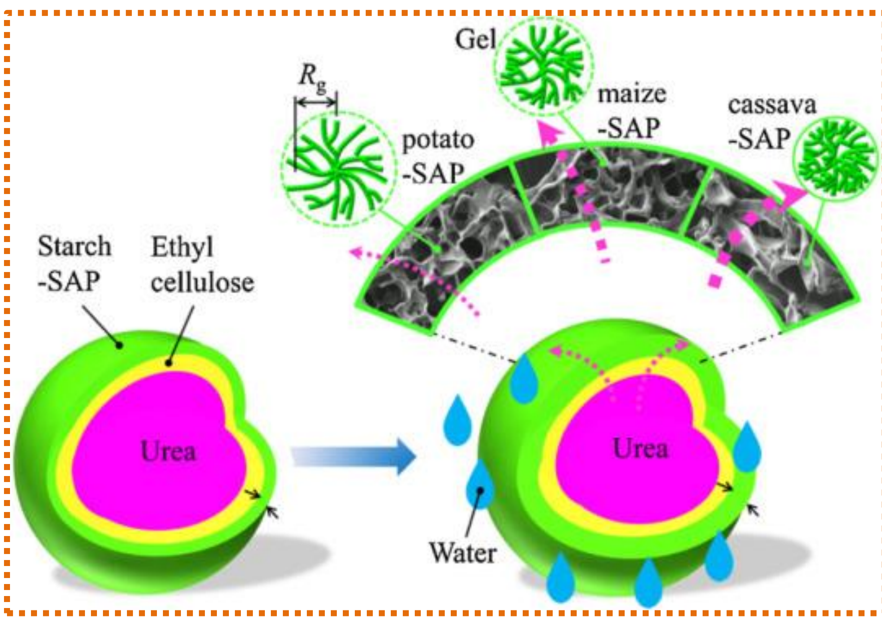

Figure 9 Controlled release of urea from agriculture hydrogel. Adopted with permission from Bahram et al.[4]

2.8.8 Plant performance

Hydrogel improves plant performance by promoting seed germination. Superabsorbent hydrogels comprised of Starch/acrylamide/ PAA /PEG exhibited positive affect on seed germination and growth of maize. Plants which were treated by hydrogels also demonstrated fresh leaves and roots with more dried weight.[116] The application of hydrogel also accelerated plant growths by increasing water holding abilities of soils predominantly in sandy soil. Konzen et al. reported that hydrogel applications increased growth, expanded collar diameter and imparted fresh organic matter under greenhouse conditions.[109] 6 g L^{-1} concentration of hydrogel improved 23% stem diameter and plant height.[117]

2.9 Controlled release fertilizers (CRFs)

Optimum supply and efficient utilization of fertilizers coupled with reduction in ecological and environmental pollution is reliant upon matching nutrients availability according to the plant requirements. Therefore, CRFs technology is opted in agronomy. CRFs sustain nutrients to the plants in delayed and controlled manner which can be regulated by their preparatory methods. A slow release fertilizer gradually release water soluble fertilizers but their release patterns and release duration are uncontrollable.[118] The use of fertilizer has tremendously amplified the rate of 5 % per year from 1950s to 1980.[119] The controlled and sustained release fertilizer is a favorite modern strategy which comprises encapsulating fertilizers in polymeric, inorganic and organic matrix. These CRFs not only enrich nutrients accessibility but also decrease soil degradation.[120] Polymers such as carrageenan, chitosan, agar, guar gum, pectin xanthan gum and alginate etc. are preferred for CRFs owing to their compatibility, environmentally friendlier, cost-affective, non-hazardous and biodegradable nature.[121] Polymer-based CRFs has many benefits such as, it curtails nutrients leaching, reduce noxiousness, permit use of more quantity of fertilizers, reduces pollution and ultimately expands agronomic safety.[113] Temperature, soil fumigation, pH, moisture content, type, nature and size of fertilizer and fillers are major factors that affect fertilizer release behaviors. The mechanism of fertilizer release from the polymer derived hydrogels is attributed to osmosis, diffusion, swelling, decomposition and chemical reaction.[113] In contrast to customary methodologies, CRFs promote availability and efficiency of the nutrients which improves crop production. Amongst hydrogels, pH and temperature are the most significant aspects that control their swelling ability which affects release of incorporated fertilizers. The soil pH directly affects the nutrient approachability. For example, some fertilizers are unsolvable at very low or high pH, which hinder fertilizers assimilation by root hairs of plants. Hereafter, pH-responsive behaviors from hydrogel avert surplus fertilizer release which has promising applications in horticulture, nurseries and agronomy. For example, Elbarbary et al. fabricated CMC/PVP superabsorbent hydrogel by gamma radiations. Hydrogel exhibited higher swelling ratio CMC/PVP 40/60. Authors also evaluated controlled release of urea, NPK and mono-potassium-phosphate (MPK) from synthesized hydrogels. The results indicated that fertilizer loaded hydrogels showed lesser swelling however, urea release was faster than that of phosphate. Morphological characterizations were carried out by using SEM demonstrated in Figure 10.[92]

Azeem et al. fabricated 3-Aminopropyl triethoxysilane (APTES) cross-linked carrageenan/PVP based polymeric, pH-sensitive environmental friendly and biodegradable hydrogel for controlled release of ammonium phosphate fertilizer.[46] The 86.82 % of the stated fertilizer was released in nine days. Shen et al. designed urea loaded halloysite nanotubes (HNTs) reinforced sodium alginate hydrogels. The result pointed out that hydrogels without HNTs presented quick urea release 60.6 %, 85.8 % and 92.6 % in 30, 120 and 240 minutes respectively. HNTs reinforced hydrogels showed relatively slower release pattern 45.6 %, 73 % and 87.8 % after 30, 120 and 240 minutes correspondingly.[122] The k-carrageenan/sodium alginate cross-linked by PAA and celite beads were also reported for controlled release of nitrogen fertilizer. The release of nitrogen fertilizer was detected 39 %, 72 % and 94% after 2nd, 5th and 25th day.[123]

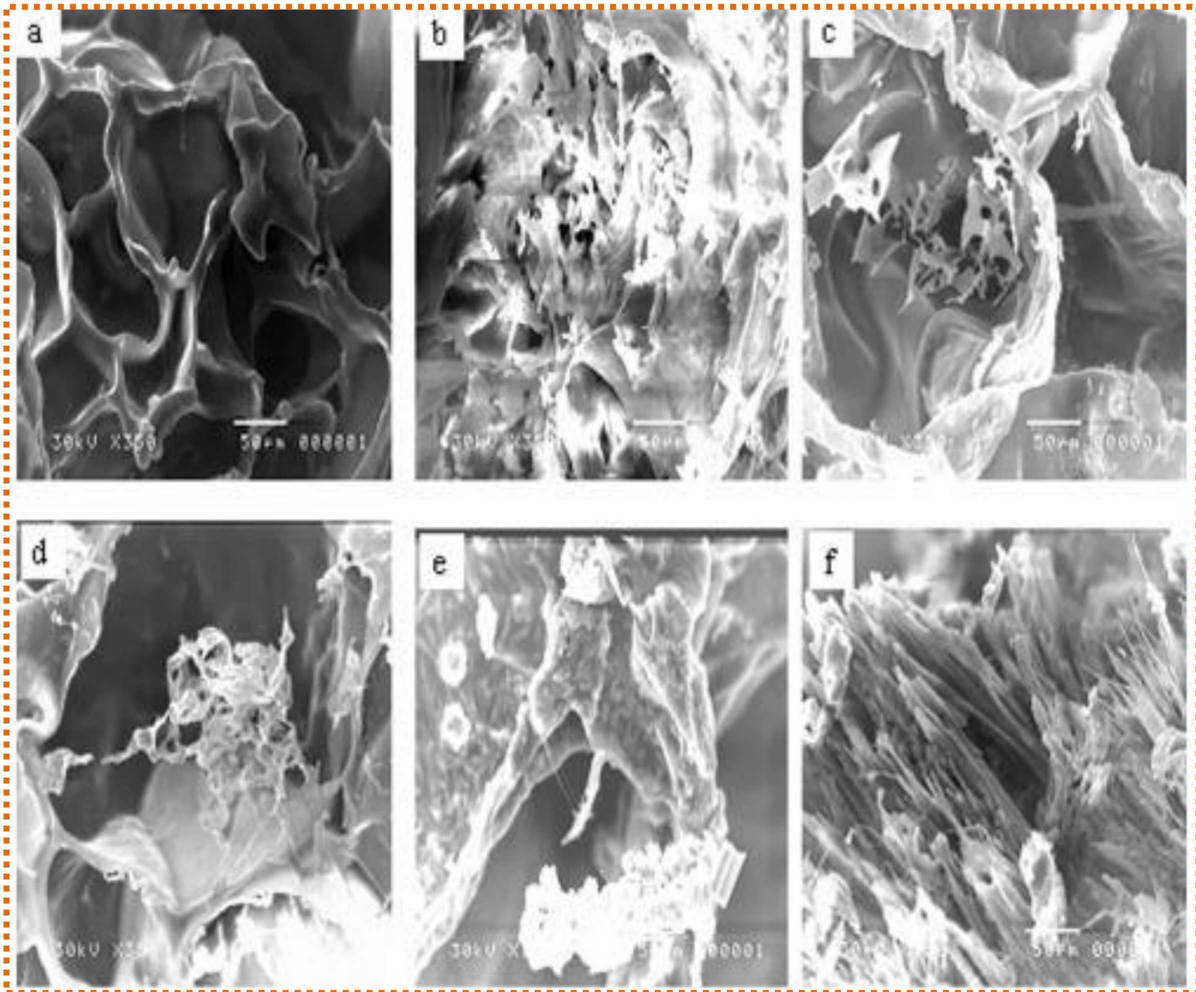

Figure 10 SEM images of CMC/PVP (40/60) hydrogel (a) without fertilizer), (b) urea loaded, (c) MKP loaded (d) NPK loaded, (e) loaded with urea, NPK and MPK (f) dried hydrogel loaded with urea, NPK and MPK adopted with permission from Elbarbary et al.[92]

Vudjung et al. reported biodegradable hydrogel fabricated by interpenetrating polymer network (IPN). The hydrogel was formulated for controlled release of nitrogen fertilizer by cross-linking cassava starch (St) and natural rubber (NR) using sulphur (S) and GA cross-linkers. Hydrogel degradation is directly proportional to NR quantity. Figure 11 presents SEM micrograph of aforesaid hydrogel for controlled release of urea.[124]

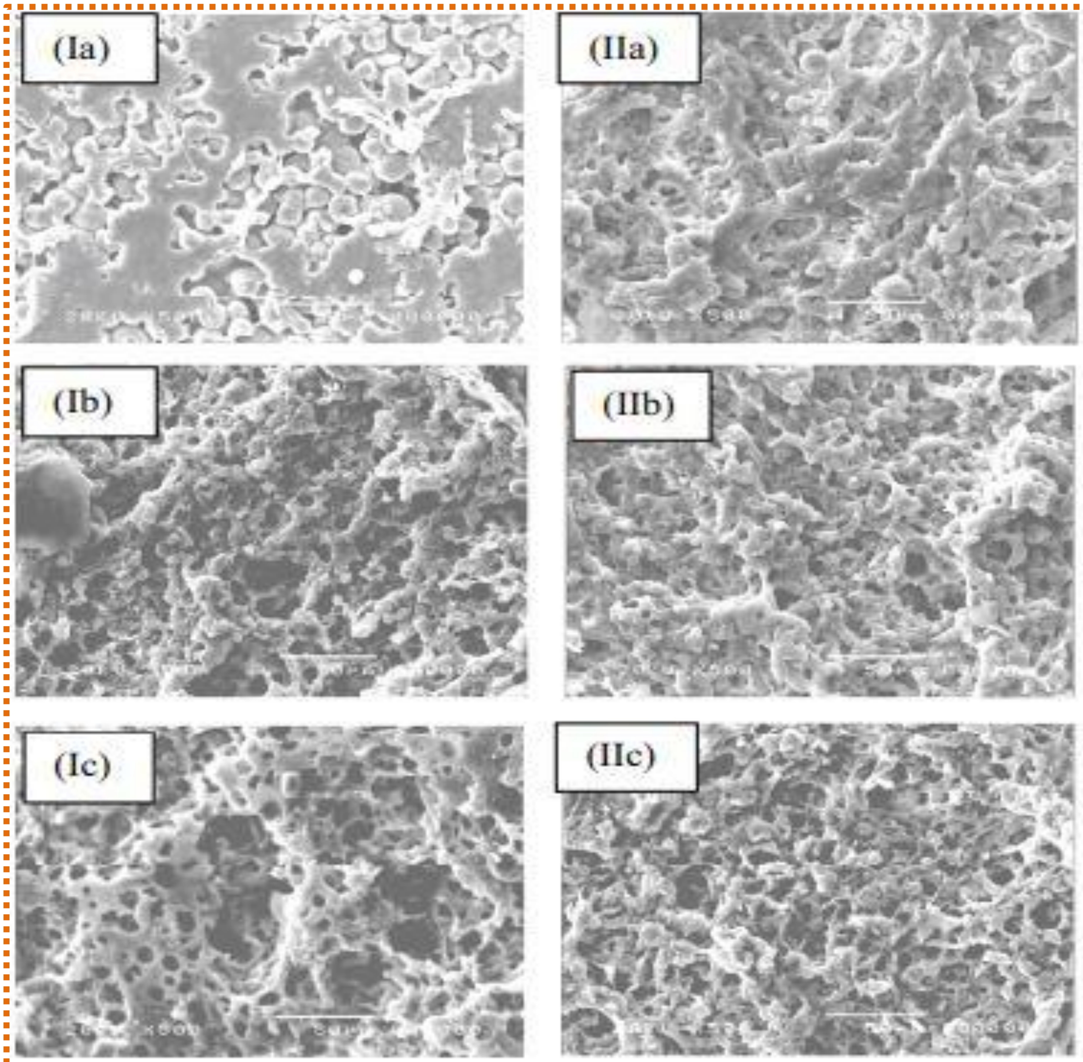

Figure 11 SEM morphological characterization of IPN/NR/St hydrogels at magnification of 500X (a) 90/10, (b) 70/30 and (c) 50/50 ratios after buried in soil for 30 (column I) and 90 days (column II) at 500 um. Adopted with permission from Vudjung et al.[124]

3 CURRENT CHALLENGES AND FUTURE PROSPECTS

Water retentive abilities of hydrogels are greatly influenced by pH. The existence of inorganic fertilizers prominently reduces water absorbing capacity. In recent times, it is vital to uplift mechanical properties, biodegradability and biocompatibility of hydrogel systems in agronomic sector. Although hydrogels face certain limitations to bear load, tensile strengths, commercialization and fertilizer loading/release. A more purposeful and precise investigations are obligatory to impart appropriate hydrophobicity, development of cost effective biodegradable agricultural hydrogels, soil degradable coatings and improvements in fertilizer loading/release profiles to alleviate these flaws to upscale and commercialize agro-based hydrogel technology. The field testing in various environmental circumstances for validation of results is also imperative.

4 CONCLUSIONS

Water is most limiting aspect for sustainment of agriculture in water strained areas. As a result, interest of scientists is growing for development of non-toxic, biocompatible and biodegradable hydrogel technologies for controlled release of fertilizers which are fabricated by physical and chemical cross-linking. In agriculture engineering, hydrogels are generally derived from polysaccharides. Water soluble polysaccharides are preferred as CRFs and soil conditioners. The temperature, radius of granules, pH and ionic strength direct their release profiles. Hydrogels uplift yield of agricultural crops by improving water holding capacity, irrigation, ensure environmental quality and competently release fertilizers. As soil conditioner hydrogels also upgrade physicochemical, hydro-physical and biological properties of soil. The combination of superabsorbent hydrogels and fertilizers in one system is valuable for improvement in efficiency and quality of soil. Hydrogels could be a practical technology to alleviate moisture and water strains from soils and enable smart and controlled release of fertilizers. Hydrogels also act as mini water-nutrient reservoirs that are available to root hairs under stress conditions. There are three steps involved in CRFs; lag phase, constant release and decay phase. Cross-linkers, binders and fillers play major role in determining properties, 3D architecture and pore sizes. Lastly, extraordinary biocompatible, cheaper, stable, biodegradable, durable, non-toxic and re-wettable characteristics of hydrogel systems governed their utilization in agronomical applications.

COMPETING INTERESTS

All authors declare no financial or personal competing interests.

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AUTHOR'S CONTRIBUTIONS

Muhammad Khalid Azeem: Data analysis, Curation, Project administration, Writing - original draft, review & editing. **Atif Islam and Rafi Ullah Khan:** Supervision, Validation, Investigation, Methodology & Data analysis & Curation. **Atta Rasool:** Conceptualization, Validation, Designing, analysis, Art work, software, Formatting, Writing - review & editing. **Muhammad Anees ur Rehman Qureshi:** Data analysis, validation, formal analysis, formatting, Writing – review & editing. **Muhammad Rizwan and Farooq Sher:** Formal analysis, validation & Curation. **Tahir Rasheed:** Supervised overall review formation.

REFERENCES

1. T. S. Daitx, M. Giovanela, L. N. Carli and R. S. Mauler, *Polymers for Advanced Technologies*, 2019, **30**, 631-639.
2. C. Kreye, B. Bouman, A. Castaneda, R. Lampayan, J. Faronilo, A. Lactaoen and L. Fernandez, *Field Crops Research*, 2009, **111**, 197-206.
3. M. Shibayama and T. Tanaka, *Responsive gels: volume transitions I*, 2005, 1-62.
4. Y. Liu, J. Wang, H. Chen and D. Cheng, *Science of the Total Environment*, 2022, 157303.
5. A. Kalhapure, R. Kumar, V. P. Singh and D. Pandey, *Current science*, 2016, 1773-1779.
6. P. Kaur, R. Agrawal, F. M. Pfeffer, R. Williams and H. B. Bohidar, *Journal of Polymers and the Environment*, 2023, 1-18.
7. M. M. Ghobashy, in *Hydrogels based on natural polymers*, Elsevier, 2020, pp. 329-356.
8. M. Bahram, N. Mohseni and M. Moghtader, in *Emerging concepts in analysis and applications of hydrogels*, IntechOpen, 2016.
9. A. S. Hoffman, *Advanced drug delivery reviews*, 2012, **64**, 18-23.
10. S. F. Kabir, P. P. Sikdar, B. Haque, M. R. Bhuiyan, A. Ali and M. Islam, *Progress in biomaterials*, 2018, **7**, 153-174.
11. M. A. u. R. Qureshi, N. Arshad, A. Rasool, A. Islam, M. Rizwan, M. Haseeb, T. Rasheed and M. Bilal, *Starch-Stärke*, 2022, 2200052.
12. J. Watanabe, Y. Kiritoshi, K. W. Nam and K. Ishihara, *Encyclopedia of Biomaterials and Biomedical Engineering*, 2004, 790-801.
13. S. B. Majee, *Emerging concepts in analysis and applications of hydrogels*, BoD–Books on Demand, 2016.
14. S. Jabeen, A. Islam, A. Ghaffar, N. Gull, A. Hameed, A. Bashir, T. Jamil and T. Hussain, *International journal of biological macromolecules*, 2017, **97**, 218-227.
15. X. Qu, A. Wirsen and A.-C. Albertsson, *Polymer*, 2000, **41**, 4589-4598.
16. S. Khan, N. Akhtar and M. U. Minhas, *Polymers for Advanced Technologies*, 2019, **30**, 755-771.
17. J. Chen, M. Liu, S. Jin and H. Liu, *Polymers for Advanced Technologies*, 2008, **19**, 1656-1663.
18. R. Teshima, Y. Kawano, T. Hanawa and A. Kikuchi, *Polymers for Advanced Technologies*, 2020, **31**, 3032-3038.
19. O. Pinkas, O. Haneman, O. Chemke and M. Zilberman, *Polymers for Advanced Technologies*, 2017, **28**, 1162-1169.
20. J. M. Unagolla and A. C. Jayasuriya, *Applied materials today*, 2020, **18**, 100479.
21. M. Naz, S. Jabeen, N. Gull, A. Ghaffar, A. Islam, M. Rizwan, H. Abdullah, A. Rasool, S. Khan and R. Khan, *Frontiers in Materials*, 2022, **9**, 826251.
22. A. Rasool, S. Ata, A. Islam and R. U. Khan, *RSC advances*, 2019, **9**, 12282-12290.
23. F. Ofridam, M. Tarhini, N. Lebaz, É. Gagnière, D. Mangin and A. Elaissari, *Polymers for Advanced Technologies*, 2021, **32**, 1455-1484.
24. J.-Y. Leong, W.-H. Lam, K.-W. Ho, W.-P. Voo, M. F.-X. Lee, H.-P. Lim, S.-L. Lim, B.-T. Tey, D. Poncelet and E.-S. Chan, *Particuology*, 2016, **24**, 44-60.
25. S. Butun, F. G. Ince, H. Erdugan and N. Sahiner, *Carbohydrate polymers*, 2011, **86**, 636-643.
26. A. Rasool, S. Ata, A. Islam, M. Rizwan, M. K. Azeem, A. Mehmood, R. U. Khan and H. A. Mahmood, *International journal of biological macromolecules*, 2020, **147**, 67-78.
27. A. Rasool, S. Ata and A. Islam, *Carbohydrate polymers*, 2019, **203**, 423-429.
28. P. B. Malafaya, G. A. Silva and R. L. Reis, *Advanced drug delivery reviews*, 2007, **59**, 207-233.
29. E. V. R. Campos, J. L. de Oliveira, L. F. Fraceto and B. Singh, *Agronomy for sustainable development*, 2015, **35**, 47-66.
30. D. Katiyar, A. Hemantaranjan and B. Singh, *Indian Journal of Plant Physiology*, 2015, **20**, 1-9.
31. G. Ma, D. Yang, Y. Zhou, M. Xiao, J. F. Kennedy and J. Nie, *Carbohydrate Polymers*, 2008, **74**, 121-126.

32. A. Rasool, M. Rizwan, A. Islam, H. Abdullah, S. S. Shafqat, M. K. Azeem, T. Rasheed and M. Bilal, *Starch-Stärke*, 2021, 2100150.
33. J. O. Bahú, L. R. M. de Andrade, R. de Melo Barbosa, S. Crivellin, A. P. da Silva, S. D. Souza, V. O. Cárdenas Concha, P. Severino and E. B. Souto, *Bioengineering*, 2022, **9**, 376.
34. H. Antoun and D. Prévost, *PGPR: biocontrol and biofertilization*, 2006, 1-38.
35. B. Qu and Y. Luo, *International Journal of Biological Macromolecules*, 2020, **152**, 437-448.
36. E. Malka, A. Dombrovsky and S. Margel, *ACS Agricultural Science & Technology*, 2022, **2**, 430-436.
37. J. Tanasić, T. Erceg, L. Tanasić, S. Baloš, O. Klisurić and I. Ristić, *Reactive and Functional Polymers*, 2021, **169**, 105085.
38. D. Venkatachalam and S. Pushparaju, 2022.
39. D. Sarmah and N. Karak, *Journal of Applied Polymer Science*, 2020, **137**, 48495.
40. H. Rodrigues Sousa, I. S. Lima, L. M. L. Neris, A. S. Silva, A. M. S. Santos Nascimento, F. P. Araújo, R. F. Ratke, D. A. Silva, J. A. Osajima and L. R. Bezerra, *Molecules*, 2021, **26**, 2680.
41. X. Li, Q. Li, X. Xu, Y. Su, Q. Yue and B. Gao, *Journal of the Taiwan Institute of Chemical Engineers*, 2016, **60**, 564-572.
42. M. Inukai, Y. Jin, C. Yomota and M. YONESE, *Chemical and pharmaceutical bulletin*, 2000, **48**, 850-854.
43. W. B. Wang and A. Q. Wang, 2010.
44. N. J. Vickers, *Current biology*, 2017, **27**, R713-R715.
45. M. K. Azeem, M. Rizwan, A. Islam, A. Rasool, S. M. Khan, R. U. Khan, T. Rasheed, M. Bilal and H. M. Iqbal, *Environmental Research*, 2022, **214**, 113790.
46. M. K. Azeem, A. Islam, M. Rizwan, A. Rasool, N. Gul, R. U. Khan, S. M. Khan and T. Rasheed, *Colloid and Polymer Science*, 2023, 1-11.
47. H. Shang, X. Yang and H. Liu, *Carbohydrate Polymers*, 2023, **313**, 120875.
48. M. S. Mutlaq and F. H. Jabrail, 2022.
49. E. Karadağ, D. Saraydin, Y. Çaldiran and O. Güven, *Polymers for Advanced Technologies*, 2000, **11**, 59-68.
50. L. Wu and M. Liu, *Polymers for Advanced Technologies*, 2008, **19**, 785-792.
51. T. d. S. Daitx, V. S. de Lima, M. Gryczak, C. L. Petzhold, L. N. Carli and R. S. Mauler, *Polymers for Advanced Technologies*, 2020, **31**, 2579-2587.
52. N. F. B. ABD GHAPAR, 2018.
53. D. Qiao, J. Li, S. Zhang and X. Yang, *Materials Today Chemistry*, 2022, **26**, 101249.
54. M. Naz, M. Rizwan, S. Jabeen, A. Ghaffar, A. Islam, N. Gull, A. Rasool, R. U. Khan, S. Z. Alshawwa and M. Iqbal, *Zeitschrift für Physikalische Chemie*, 2022, **236**, 227-238.
55. T. T. Zhu, C. H. Zhou, F. B. Kabwe, Q. Q. Wu, C. S. Li and J. R. Zhang, *Applied Clay Science*, 2019, **169**, 48-66.
56. J. Yin, F. Zhan, T. Jiao, H. Deng, G. Zou, Z. Bai, Q. Zhang and Q. Peng, *Chinese Chemical Letters*, 2020, **31**, 992-995.
57. L. M. Sanchez, P. S. Shuttleworth, C. Waiman, G. Zanini, V. A. Alvarez and R. P. Ollier, *Journal of Environmental Chemical Engineering*, 2020, **8**, 103795.
58. M. Rizwan, V. Selvanathan, A. Rasool, M. A. U. R. Qureshi, D. N. Iqbal, Q. Kanwal, S. S. Shafqat, T. Rasheed and M. Bilal, *Water, Air, & Soil Pollution*, 2022, **233**, 493.
59. S. K. Patra, R. Poddar, M. Brestic, P. U. Acharjee, P. Bhattacharya, S. Sengupta, P. Pal, N. Bam, B. Biswas and V. Barek, *International Journal of Polymer Science*, 2022, **2022**.
60. R. Vundavalli, S. Vundavalli, M. Nakka and D. S. Rao, *Procedia Materials Science*, 2015, **10**, 548-554.
61. A. Rehman, R. Ahmad and M. Safdar, *Plant, Soil and Environment*, 2011, **57**, 321-325.
62. M. Bakass, A. Mokhlisse and M. Lallemant, *Journal of applied polymer science*, 2002, **83**, 234-243.

63. M. Liu, R. Liang, F. Zhan, Z. Liu and A. Niu, *Polymer international*, 2007, **56**, 729-737.
64. M. S. Johnson, *Journal of the Science of Food and Agriculture*, 1984, **35**, 1196-1200.
65. T. Neethu, P. Dubey and A. Kaswala, *Int. J. Curr. Microbiol. App. Sci*, 2018, **7**, 3155-3162.
66. D. Peterson, 2002.
67. E. M. Ahmed, *Journal of advanced research*, 2015, **6**, 105-121.
68. D. Krein, M. Rosseto, F. Cemin, L. Massuda and A. Dettmer, *International Journal of Environmental Science and Technology*, 2023, 1-16.
69. S. I. Sempeho, H. T. Kim, E. Mubofu and A. Hilonga, 2014.
70. S. A. Irfan, R. Razali, K. KuShaari, N. Mansor, B. Azeem and A. N. F. Versypt, *Journal of Controlled Release*, 2018, **271**, 45-54.
71. D. Lawrencia, S. K. Wong, D. Y. S. Low, B. H. Goh, J. K. Goh, U. R. Ruktanonchai, A. Soottitantawat, L. H. Lee and S. Y. Tang, *Plants*, 2021, **10**, 238.
72. S. Ata, A. Rasool, A. Islam, I. Bibi, M. Rizwan, M. K. Azeem and M. Iqbal, *International journal of biological macromolecules*, 2020, **155**, 1236-1244.
73. S. Basu, N. Kumar and J. Srivastava, *Simulation Modelling Practice and Theory*, 2010, **18**, 820-835.
74. M. Salimi, E. Motamedi, B. Motesharezedeh, H. M. Hosseini and H. A. Alikhani, *Journal of Environmental Chemical Engineering*, 2020, **8**, 103765.
75. A. Olad, H. Zebhi, D. Salari, A. Mirmohseni and A. R. Tabar, *Materials Science and Engineering: C*, 2018, **90**, 333-340.
76. A. Rasool, M. Rizwan, T. Rasheed and M. Bilal, in *Smart Polymer Nanocomposites*, Elsevier, 2023, pp. 219-240.
77. C.-w. Du, J.-m. Zhou and A. Shaviv, *Journal of Polymers and the Environment*, 2006, **14**, 223-230.
78. N. Emami, A. Razmjou, F. Noorisafa, A. H. Korayem, A. Zarrabi and C. Ji, *Environmental nanotechnology, monitoring & management*, 2017, **8**, 233-243.
79. S. Bi, V. Barinelli and M. J. Sobkowicz, *Polymers*, 2020, **12**, 301.
80. C. Feng, S. Lü, C. Gao, X. Wang, X. Xu, X. Bai, N. Gao, M. Liu and L. Wu, *ACS Sustainable Chemistry & Engineering*, 2015, **3**, 3157-3166.
81. P. Wen, Y. Han, Z. Wu, Y. He, B.-C. Ye and J. Wang, *Arabian Journal of Chemistry*, 2017, **10**, 922-934.
82. J. F. E. Andes, A. F. Jao, J. H. Zacarias and T. Tumolva, 2021.
83. R. Rajakumar and J. Sankar, *Int. J. Appl. Pure Sci. Agric*, 2016, **2**, 163-172.
84. J. Fulton.
85. A. Shaviv, S. Raban and E. Zaidel, *Environmental science & technology*, 2003, **37**, 2251-2256.
86. Y. Oladosu, M. Y. Rafii, F. Arolu, S. C. Chukwu, M. A. Salisu, I. K. Fagbohun, T. K. Muftaudeen, S. Swaray and B. S. Haliru, *Horticulturae*, 2022, **8**, 605.
87. P. Solanki, A. Bhargava, H. Chhipa, N. Jain and J. Panwar, *Nanotechnologies in food and agriculture*, 2015, 81-101.
88. H. Cui, C. Sun, Q. Liu, J. Jiang and W. Gu, 2010.
89. E. Corradini, M. De Moura and L. Mattoso, *Express polymer letters*, 2010, **4**.
90. D. Sun, H. I. Hussain, Z. Yi, R. Siegele, T. Cresswell, L. Kong and D. M. Cahill, *Plant cell reports*, 2014, **33**, 1389-1402.
91. E. Navarro, A. Baun, R. Behra, N. B. Hartmann, J. Filser, A.-J. Miao, A. Quigg, P. H. Santschi and L. Sigg, *Ecotoxicology*, 2008, **17**, 372-386.
92. A. M. Elbarbary and M. M. Ghobashy, *Radiochimica Acta*, 2017, **105**, 865-876.
93. M. M. Ghobashy, B. K. El-Damhougy, H. A. El-Wahab, M. Madani, M. A. Amin, A. E. M. Naser, F. Abdelhai, N. Nady, A. S. Meganid and S. A. Alkhursani, *Polymers for Advanced Technologies*, 2021, **32**, 514-524.

94. M. Guo, M. Liu, F. Zhan and L. Wu, *Industrial & engineering chemistry research*, 2005, **44**, 4206-4211.
95. J. Sharma, B. Kaith and M. Bhatti, *Journal of Polymers and the Environment*, 2018, **26**, 518-531.
96. T. Jamnongkan and S. Kaewpirom, *Journal of Polymers and the Environment*, 2010, **18**, 413-421.
97. Y.-C. Chen and Y.-H. Chen, *Science of the Total Environment*, 2019, **655**, 958-967.
98. R. C. Gonçalves, D. P. da Silva, R. Signini and P. L. F. Naves, *International journal of biological macromolecules*, 2017, **105**, 385-392.
99. A. Singh, D. J. Sarkar, S. Mittal, R. Dhaka, P. Maiti, A. Singh, T. Raghav, D. Solanki, N. Ahmed and S. B. Singh, *Journal of Applied Polymer Science*, 2019, **136**, 47332.
100. S. Liu, Q. Wu, X. Sun, Y. Yue, B. Tubana, R. Yang and H. N. Cheng, *International Journal of Biological Macromolecules*, 2021, **172**, 330-340.
101. W. Zhao, B. Bai, Z. Hong, X. Zhang and B. Zhou, *ACS omega*, 2020, **5**, 24838-24847.
102. W.-x. Jiang, J.-R. Qi, J.-s. Liao and X.-Q. Yang, *International Journal of Biological Macromolecules*, 2022, **208**, 486-493.
103. A. Bortolin, F. A. Aouada, L. H. Mattoso and C. Ribeiro, *Journal of agricultural and food chemistry*, 2013, **61**, 7431-7439.
104. O. El-Hady, S. Abo-Sedera, A. Basta and H. El-Saied, *Bio*, 2011, **1**, 78-84.
105. W. He, L. Jing-Jing, W. Hong-liang, W. Gang, C. Hui-Juan and Z. Jing, *Journal of Light Industry*, 2017, **32**.
106. C. Adams, J. Frantz and B. Bugbee, *Journal of plant nutrition and soil science*, 2013, **176**, 76-88.
107. J. Oertli and O. Lunt, *Soil Science Society of America Journal*, 1962, **26**, 579-583.
108. R. A. Meurer, S. Kemper, S. Knopp, T. Eichert, F. Jakob, H. E. Goldbach, U. Schwaneberg and A. Pich, *Angewandte Chemie International Edition*, 2017, **56**, 7380-7386.
109. E. R. Konzen, M. C. Navroski, G. Friederichs, L. H. Ferrari, M. d. O. Pereira and D. Felippe, *Cerne*, 2017, **23**, 473-482.
110. N. Gokavi, K. Mote, D. Mukharib, A. Manjunath and Y. Raghuramulu, *Journal of Pharmacognosy and Phytochemistry*, 2018, **7**, 1364-1366.
111. N. Thombare, S. Mishra, M. Siddiqui, U. Jha, D. Singh and G. R. Mahajan, *Carbohydrate polymers*, 2018, **185**, 169-178.
112. M. Barakat, S. El-Kosary, T. Borham and M. Abd-ElNafea, *Journal of Horticultural Science & Ornamental Plants*, 2015, **7**, 19-28.
113. M. Rajan, S. Shahena, V. Chandran and L. Mathew, in *Controlled release fertilizers for sustainable agriculture*, Elsevier, 2021, pp. 41-56.
114. S. Shoji and H. Kanno, *Fertilizer Research*, 1994, **39**, 147-152.
115. F. Wang and A. Alva, *Soil Science Society of America Journal*, 1996, **60**, 1454-1458.
116. N. M'barki, H. Chehab, F. Aissaoui, O. Dabbaghi, F. Attia, Z. Mahjoub, S. Laamari, B. Chihaoui, T. del Giudice and A. Jemai, *Acta Physiologiae Plantarum*, 2018, **40**, 1-10.
117. M. R. Bernardi, M. Sperotto Junior, O. Daniel and A. C. T. Vitorino, *Cerne*, 2012, **18**, 67-74.
118. H. M. Jalil, S. Rezapour, A. Nouri and N. Joshi, *Agricultural Water Management*, 2022, **272**, 107848.
119. A. Shaviv, in *Optimization of Plant Nutrition*, Springer, 1993, pp. 651-656.
120. A. Shaviv, 2001.
121. A. Pourjavadi, M. Sadeghi and H. Hosseinzadeh, *Polymers for advanced technologies*, 2004, **15**, 645-653.
122. Y. Shen, H. Wang, W. Li, Z. Liu, Y. Liu, H. Wei and J. Li, *International journal of biological macromolecules*, 2020, **164**, 557-565.
123. Y. Wang, M. Liu, B. Ni and L. Xie, *Industrial & Engineering Chemistry Research*, 2012, **51**, 1413-1422.
124. C. Vudjung and S. Saengsuwan, *Journal of Polymers and the Environment*, 2018, **26**, 3967-3980.