AGRICULTURAL BIOLOGY,
2023, V. 58, Iss. 1, pp. 23-42
[SEL'SKOKHOZYAISTVENNAYA BIOLOGIYA]

ISSN 2412-0324 (English ed. Online)
ISSN 0131-6397 (Russian ed. Print)
ISSN 2313-4836 (Russian ed. Online)

UDC 631.4:631.617:631.672:631.81

doi: 10.15389/agrobiology.2023.1.23eng
doi: 10.15389/agrobiology.2023.1.23rus

POLYMER HYDROGELS IN AGRICULTURE
(review)

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The authors declare no conflict of interests
Acknowledgements:
The work was supported financially by the Government of the Perm Territory within the framework of scientific project No. S-26/507.
Final revision received July 27, 2022
Accepted August 26, 2022

Abstract

Polymer hydrogels (PHGs) are formed by swelling three-dimensionally cross-linked hydrophilic polymers and are usually characterized by high water-holding capacity (K. Rop et al., 2019; N. Singh et al., 2021; A. Sikder et al., 2021). Moisture capacity and a prolonged release of fertilizers, pesticides and bio-preparations make them promising for use in agriculture (P. Rychter et al., 2016; A. Sikder et al., 2021). PHGs reduces the need for frequent irrigation, increases seed germination, plant growth, seedling survival, enhances root growth, prevents soil erosion, pesticide and fertilizer overdose (N. Singh et al., 2021). According to their origin, PHGs are divided into synthetic and natural ones: synthetic hydrogels, mainly polymers and copolymers of acrylamide and acrylic acid, have a high water-holding capacity and strength, however, they are weakly degraded in soils (A.V. Smagin et al., 2014; B. Wilske et al., 2014). It is known that microorganisms are able to use PHGs based on acrylic polymers as a source of nitrogen and/or carbon for growth (H. Matsuoka et al., 2002; M. Bao et al., 2010; F. Yu et al., 2015) due to the presence of amidase activity (F. Yu et al., 2015; A. Nyyssцlд et al., 2019), ensuring gradual decomposition of PHGs in the soil. Natural hydrogels, among which cellulose-based PHGs predominate, have less strength, but are biodegradable and are environmentally friendly (R. Kundu et al., 2022). In addition to cellulose, collagen (Z.-Y. Hu et al., 2021), alginates (B. Tomadoni et al., 2020), chitosan (A. Zinchenko et al., 2022), and other polysaccharides are used as water-retaining strongly swelling agents of natural origin. Hydrogels are promising as carriers for the prolonged release of fertilizers, mainly urea (P. Rychter et al., 2016; W. Tanan et al., 2021), pesticides (C. Xu et al., 2021; C. Bai et al., 2015; F.E. Baloch et al., 2021; D. Zheng et al., 2022), for the introduction of microbial preparations into the soil, including phosphate-mobilizing and nitrogen-fixing bacteria (C.S. Wu, 2008; A.V. Kovrizhnikov et al., 2021). For a more active introduction of PHGs into practice, it is necessary to reduce their cost, mainly by the creation of composite materials based on agricultural and biotechnology industries waste. It is necessary to combine the positive qualities of synthetic and natural PHGs, synthesizing semi-synthetic hydrogels that are biodegradable and do not pollute the environment, have optimal mechanical strength and water-absorbing capacity. As water-retaining and anti-erosion agents, hydrogels based on polymers and copolymers of acrylamide and acrylic acid are more promising (I.G. Panova et al., 2021; N.B. Sadovnikova et al., 2014; A.V. Smagin et al., 2014), and natural and semi-synthetic PHGs are more promising as carriers of fertilizers and pesticides (P. Jungsinyatam et al., 2022; A. Di Martino et al., 2021). This review summarizes current information on the use of PHGs of various compositions in agriculture, provides data on the positive effect of PHGs on soil water balance, productivity, growth, survival of various crops, seed germination and commercial quality of root crops, as well as the prospects for the PHGs development.

Keywords: polymer hydrogels, water-retaining capacity, biological preparations, fertilizers, pesticides

Hydrophilic polymers with multiple bonds between macromolecules can

absorb water volume exceeding their own dry mass 1000-fold or more. The resulting polymer hydrogels (PHGs) retain their swollen state even under pressure. The ability to absorb and retain water is due to the presence of hydrophilic groups −OH, −CONH−, $-CONH_2$, $-SO_3H$, $-NH_2$, −COOH, −OH in the polymer molecule. Despite their high moisture holding capacity, PHGs do not dissolve due to their three-dimensionally cross-linked structure [1, 2].

The purpose of this review is to summarize and analyze data regarding the use of hydrophilic polymers in agriculture, to show their advantages and problems when introduced into practice, and to provide examples of application.

In agriculture, hydrogels are used for several purposes. Firstly, in crop production, their superabsorbent qualities are realized, mainly moisture capacity, the ability to retain and gradually release water; secondly, hydrogels can be carriers for minerals, growth stimulants, and pesticides; thirdly, biological products are introduced into the soil with hydrogels.

PHGs are soil conditioners that improve its physical and chemical properties, and therefore fertility. By serving as a water reservoir near the plant root zone, hydrogels reduce soil osmotic pressure and improve water supply, with 95% of the water absorbed by the hydrogel remaining available to the plant [3]. Upon PHG incorporation of into the soil, ventilation and root development, the viability of plants in general, the rate of seed germination, productivity increase, and, as a result, the cost of crop production decreases [2, 4]. PHGs are used as water-retaining agents in agriculture in arid regions, as well as in urban landscape and home gardens, and are used to improve the survival rate of seedlings [5]. PHGs prevent crusting and soil erosion on irrigated lands [6, 7]. Hydrogels are promising in soil-free cultivation technologies, when growing plants hydroponically on vermiculite, perlite, sand and other substrates [8]. In addition, hydrogels serve as a material for encapsulating mineral fertilizers [9, 10], promote their gradual release into soils and provide a prolonged effect [11-13].

Figure 1 shows various applications of PHGs in agriculture.

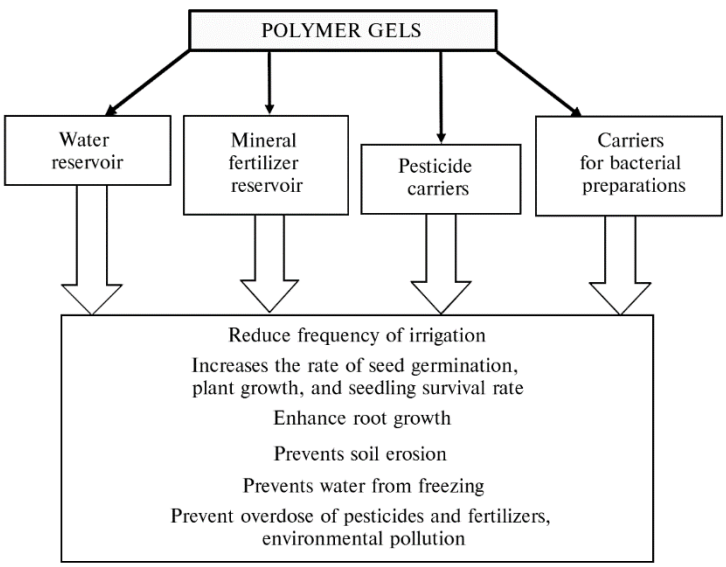

Fig. 1. Application of polymer hydrogels in agriculture.

Classification of hydrogels. Methods of obtaining. Physicochemical characteristics. According to their origin, PHGs are synthetic and natural. Synthetic PHGs are characterized by significant water absorption capacity, long shelf life and fairly high mechanical strength. In turn, natural

materials are safe for the environment, have better biodegradability, but at the same time they have less mechanical strength and moisture retention [1, 14, 15].

Synthetic polyacrylamide and polyacrylate hydrogels. Among the numerous soil conditioners used in practice to optimize the physical state of soils, hydrophilic highly swelling polymer hydrogels based on polyacrylamide and polyacrylates are of particular interest. Such hydrogels have a very high degree of swelling in water (up to 1000 g H_2O/g dry polymer) and are effectively used to regulate the water-holding capacity of light-textured soils [16].

To obtain synthetic hydrogels, acrylamide and acrylic acid are mainly used. Chemical cross-linking of polymers is accomplished through various methods, such as free radical polymerization, condensation polymerization, ultraviolet irradiation, and small-molecule cross-linking [17].

Acrylamide-based hydrogels are the most commonly used. They are capable of significant changes in volume in response to physical and chemical influences. Polyacrylamide hydrogels are traditionally produced by free radical polymerization, the initiation process of which uses a combination of ammonium persulfate and tetramethylethylenediamine. Free radicals, which are formed from the initiator, break double bonds in monomers. In addition, these radicals act on the double bond of the crosslinking agent N,N′-methylene-bis-acrylamide, resulting in the formation of covalent bonds between it and the monomers. The hydrolytic stability of the gel (the ability to resist chemical degradation in the presence of water) can be further improved by the introduction of acrylamides with groups such as alkyl and hydroxyalkyl [17].

Acrylic acid contains a vinyl radical connected to a carboxyl group, which ensures a reaction with electrophilic agents and free radicals. Polyacrylates are synthesized by free radical polymerization from acrylic acid monomers or by their combination with other monomers. Polymerization of acrylic acid can also occur in an acidic environment using sulfuric acid and chlorosulfonic acid. In addition, polymerization is possible in the presence of alkalis, iron salts, high temperature, light, and peroxide compounds [17].

Polyacrylamide derivatives are divided into cationic, anionic, nonionic and polyampholytes. An additional stabilizing effect can be achieved by binding anionic and cationic polymers. Such an interpolyelectrolyte complex is stabilized by the electrostatic interaction of cationic and anionic units and contains hydrophobic and hydrophilic segments. The former are represented by blocks with mutually neutralized charges of both polymers, the latter by free fragments of polymer chains. Modification of an anionic hydrogel with a linear cationic polymer increases the strength of polymer-soil formations, only slightly reducing the ability of the hydrogel to swell and retain moisture. Micro-sized hydrogels of this type seem to be the most promising for suppressing erosion processes in the soil and creating favorable conditions for plant development, especially in areas with insufficient moisture [7].

When synthetic polyacrylate and polyacrylamide hydrogels were added in doses of 0.2-0.3%, an increase in the water-holding capacity of soils of different genesis, composition and dispersion and a heavier granulometric composition were revealed, and the greatest effect was achieved in non-saline sandy substrates. In this case, water retention increased 3-5 times, reaching the level in natural sandy loams and loams [18].

Degradation of PHGs in soils is one of the main factors limiting its effectiveness. Biodegradation depends on climatic conditions and soil type. Thus, in humid climatic conditions, the PHG destruction proceeds more slowly than in arid irrigated soils, and 10-13% of the applied amount is lost during the growing season. The greatest stability of PHG is observed at 20 °C, while the period of

95% decomposition of the hydrogel introduced at a concentration of 0.05-0.2% is 2-15 years, respectively, while at 37 °C it is 1.7-7.5 years [19].

Hydrogels based on biopolymers. Superabsorbent hydrogels can be synthesized based on polysaccharides - cellulose, starch, guar gum, cyclodextrin, xanthan [15, 20, 21], alginate, chitosan, κ-carrageenan [22-24]. Biodegradability, biocompatibility, non-toxicity and insolubility in most solvents, as well as the ability to be obtained from natural and renewable raw materials, make cellulose an attractive source for hydrogel production. Cellulose hydrogels are used in agriculture due to their superabsorbent properties and environmental friendliness. They are usually synthesized by free radical polymerization using cellulose derivatives such as carboxymethylcellulose (CMC) and its sodium salt [25]. Cellulose-based PHGs can be synthesized from lignocellulosic biomass, rice straw, pulp and paper industry waste, and agricultural waste [25-27]. In the structure of plant cellulose, elementary fibrils are distinguished, organized into larger microfibrils. Plant cellulose is a crystallizable polymer with crystalline and amorphous parts [28]. In addition, PHG can be obtained from bacterial cellulose, in which case the material has a number of advantages over cellulose hydrogels of plant origin due to its crystalline nanofibrillar structure, which increases its strength. Cellulose of this type is produced extracellularly by representatives of the genus *Gluconacetobacter* and some other bacteria, and is characterized by high purity, since it does not contain hemicellulose and lignin, tensile strength, and greater water-holding capacity. On average, the length of a nanofiber is 100-1000 nm, its diameter is 20-100 nm, and its crystallinity is 50-60% [29].

In addition to the function of swelling and water retention, cellulose-based PHGs can perform the function of slow release of some nitrogen fertilizers. Thus, an anionic hydrogel was synthesized from cellulose nanofibers oxidized with 2,2,6,6-tetramethyl-1-piperidinyloxy radical in an aqueous solution of NaOH/urea and epichlorohydrin as a cross-linker. This hydrogel had a microporous structure and high hydrophilicity, excellent water absorption properties with controlled release of urea, and supported the process of seed germination and plant growth [30].

A hydrogel fertilizer based on skin waste has been proposed for the controlled release of mineral matter. The addition of skin waste hydrolyzate promoted the formation of a porous structure without any subsequent treatment or the use of a special porogen. This hydrogel had a high swelling rate and was biodegradable by microorganisms in the soil, which led to the gradual release of fertilizer when growing plants. The collagen-based hydrogel fertilizer demonstrated high water absorption capacity reaching 2208 g/g, as well as controlled release of nitrogen and potassium for more than 40 days [31].

Sodium alginate is a biopolymer of natural origin, a linear polysaccharide consisting of (1-4)-linked residues β-D-mannuronate and α-L-guluronate with two main functional groups (—COOH and —OH), which is hydrophilic, biocompatible and biodegradable. Calcium cations bind guluronic acid residues through carboxyl groups, which leads to gelation. $CaCl_2$ concentration and cross-linking time were the most important variables affecting the swelling properties of alginate-based hydrogels. The degree of swelling of the alginate hydrogel prepared from a 2-3% alginate solution cross-linked with 0.2% $CaCl_2$ for 10 minutes was 55 g of distilled water per 1 g of dry hydrogel in 24 hours. The experiment demonstrated the ability of this PHG to control soil moisture and support lettuce growth under drought conditions [32].

To prevent wind and water erosion of soil, a method was developed based on in situ gelation of a polyion complex formed from chitosan and CMC. This gel was prepared by sequentially adding chitosan powder and D-(+)-glucono- -

lactone to a 1% CMC solution with vigorous stirring. Hydrolysis of the acidifying agent, glucono-δ-lactone, reduces the pH of the dispersion from neutral to slightly acidic, initiating the gradual dissolution of chitosan caused by the protonation of its amino groups. Gradually dissolving cationic chitosan electrostatically interacts with negatively charged CMC and forms a CMC-chitosan polymer network. Soil particles formed a composite with polymer films and microfibers through electrostatic interactions. The mechanical properties of such soils depended on the structure and stability of the polyionic network of carboxymethylcellulose and chitosan and were controlled by the degree of polymerization of macromolecules. The hydrogel-like polymer network has been shown to be equally suitable for mechanical amendment of soil containing large amounts of water and dry soil material [33].

Hydrogels of mixed nature (a semi-synthetic PHG). When using synthetic materials as carriers for fertilizers, two main disadvantages can be noted: firstly, non-renewable resources are used to obtain them, and secondly, the remains of the covering shells are not biodegradable and can be potentially harmful to the soil environment. In this regard, there is a need for inexpensive biodegradable materials based on renewable resources that provide controlled release of mineral fertilizers [34, 35]. Macromolecules of natural origin are copolymerized with chemical compounds to improve the technical characteristics of polymer networks and are used for moisture retention and prolonged release of nutritional compounds and plant protection products [36-39]. New commercially available biodegradable copolymers of cassava starch, acrylic acid, natural rubber and vinyl alcohol (VA) were developed by varying the ratio of starch to acrylic acid, but with a fixed ratio of rubber to VA. Properties of this material include good water retention, high swelling ability, acceptable thermal stability, and satisfactory biodegradability [40]. As the rubber to VA ratio increases, the tensile strength, water absorption, and biodegradability of hydrogels tend to decrease, but advantages such as higher thermal stability and denser structure emerge. These hydrogels have been used to slowly release urea [41].

Superabsorbent composites based on sugarcane bagasse (bagasse), polyacrylamide and attapulgite have been developed for controlled release of urea. The composites were prepared by graft copolymerization of acrylamide on bagasse in the presence of attapulgite using N,N′-methylene-bis-acrylamide as a cross-linker and potassium persulfate as a polymerization initiator [42].

For planting guava under drought conditions, PHGs based on a natural product, guar gum, covalently cross-linked with various acrylate monomers (acrylamide, acrylic acid and N-isopropylacrylamide) was used [43], and for planting sugar cane, PHG based on guar gum with polyethylene glycol [44]. The hydrogel composite with urea and biochar obtained by slow pyrolysis of switchgrass had a high water absorption capacity and ensured the gradual release of nitrogen. To prepare PHG, urea, cellulose, acrylamide, potassium persulfate, N,N′-methylene-bis-acrylamide, biochar (2.5-7.5%) were mixed, purged with nitrogen gas and irradiated in a microwave oven at a power of 495-825 W. There was no obvious cross-linking between the biochar and other materials in the composite, and the urea-bound biochar was gradually released during the swelling of the composite. The water absorption capacity increased with increasing biochar dosage. When applied to soil, such composites can release nutrients along with some of the biochar while increasing soil moisture [45]. A hydrogel based on cellulose extracted from sugarcane pulp with sulfuric acid and sodium hydroxide, modified with polyvinyl alcohol and the cross-linking agent glutaraldehyde, quickly swelled (compared to regenerated cellulose without additives), had a structure resistant to mechanical destruction, and the ability to biodegrade. The swelling rate was 135% [46].

PHGs synthesized from cellulose, acrylamide and acrylic acid provided controlled release of urea and calcium superphosphate. These fertilizer granules were sprayed with a solution of epoxy resin in acetone to improve the adhesion of the hydrogel, after which the hydrogel was sprayed to obtain a two-layer coating. The combined PHG had a high swelling ratio (88.8%) and not only released nutrients but also increased water availability to plants [47].

Copolymerization of starch with acrylamide or acrylic acid provides production of superabsorbents with high water absorption capacity. Graft copolymerization is a widely used chemical method for preparing starch-based hydrogels. Starch molecules and monomers of acrylamide or acrylic acid are covalently grafted under the action of an initiator (potassium persulfate) and a cross-linking agent N,N′-methylene-bis-acrylamide.

Starch-grafted acrylamide hydrogel swelled up to 905% at pH 11 [48]. Superabsorbents based on modified carboxymethylated corn starch and partially neutralized acrylic acid were obtained by radical copolymerization of its monomers and modified starch in a parts ratio of 3.75:1. With the highest degree of carboxymethylation of starch and a decrease in the concentration of the crosslinking agent N,N′-methylene-bis- acrylamide from 0.0480 to 0.0047 mol% water absorption increased from 232 to 1203 g/g, that is, the amount of absorbed water increased with decreasing amount of cross-linking agent [49].

Problems of biodestruction of PHG. Polymer hydrogels, including those based on polymers and copolymers of polyacrylamide and polyacrylic acid, when added to soils, should perform the function of retaining moisture and gradually supplying plants with water, but at the same time undergo gradual decomposition in the soil without polluting the environment. When using gels based on polymers and copolymers of acrylamide and acrylic acid, this is especially true because the monomers acrylamide and acrylic acid are highly toxic to living organisms [50-52]. The question arises whether such gels will undergo decomposition with the release of monomers and whether their degradation is exclusively a physicochemical process or is supplemented by biodegradation with the participation of microorganisms.

In the biodegradation of polymers, the following stages can be distinguished: fragmentation of polymers under the influence of various physical, chemical and biological factors; the formation of oligomers, dimers and monomers under the influence of microbial enzymes; penetration of small molecules into the cytoplasm of microbial cells; bioassimilation, i.e., integration of molecules into microbial metabolism to obtain energy and synthesize new biomass macromolecules; mineralization, i.e., the release of simple and complex metabolites into the environment, the release of water and simple compounds of carbon and nitrogen [53].

To date, microbial degradation of polyacrylamide and polyacrylate gels remains poorly studied. It is known that the structural stability of superabsorbent polymers increases with increasing density of three-dimensional cross-links [17]. It was reported that polyacrylate PHGs are practically not biodegraded and the polyacrylate backbone decomposes in loamy soils at a rate of no more than 0.12-0.24% in 6 months [54]. However, there is an opposing view that these synthetic hydrogels undergo physicochemical degradation, after which short stretches of the polymer are destroyed by soil microbiota [19, 55]. The limited information on bacterial strains that degrade polyacrylamide confirms the possibility of microorganisms using this polymer as a source of carbon and nitrogen and its complete utilization [56-58] or carbon [56, 59-61] for growth. Obviously, the possibility of utilizing polyacrylamide as a source of energy and/or nitrogen nutrition is associated with the presence of amidase activity [61-63]. It has been shown that among

eukaryotic organisms, only the white rot pathogen *Phanerochaete chrysosporium* can use polyacrylamide and polyacrylate as a source of carbon and nitrogen. Apparently, these polymers are destroyed by enzymes that oxidize lignin (in particular, peroxidases), and subsequently the formation of soluble polymer degradation products, the hydroxylated derivatives of carboxylic acids and amino derivatives occurs with their further use as a substrate and mineralization by prokaryotes and plants. Toxic acrylic derivatives are not formed in this case [63, 64].

Hydrogels based on biopolymers are decomposed by enzymes of soil microorganisms. Starch is mainly broken down by glycoside hydrolases, a large group of enzymes that catalyze the hydrolysis of glycosidic bonds. The α-amylase performs the primary cleavage of long starch polymers to form shorter fragments, which are then hydrolyzed by β-amylase, glucoamylase and α-glucosidase. Starch hydrolyzing enzymes are present in a variety of soils and are produced by both bacteria and fungi. In addition to glycoside hydrolases, polysaccharide monooxygenases are capable of oxidative degradation of starch [65]. Cellulase enzymes, which catalyze the cleavage of β-glycosidic bonds, are responsible for the degradation of extracellular cellulose. There are endoglucanases, which hydrolyze the internal bonds of cellulose, and cellobiohydrolases, which attack only the terminal groups. These enzymes are produced by cellulolytic microorganisms, which are dominated by fungi and eubacteria [66].

Chitosan and alginate are also subject to biodegradation. Depolymerization of chitosan is carried out by hydrolases — highly specific chitosanases and nonspecific enzymes such as lipases and cellulases. Microbial chitosanases are extracellular inducible enzymes secreted into the environment by both bacteria and fungi [67]. Alginate lyases are also widespread in nature: they are synthesized in seaweeds, invertebrates, bacteria, and fungi. Endoalginate lyases are divided into polyguluronate lyases, polymannuronate lyases, and bifunctional alginate lyases, which are specific for 1→4-glycosidic bonds between both mannuronic and guluronic acid residues. Exoalginate lyases (oligouronide lyases) break down alginic acid oligosaccharides to monosaccharides [68].

Thus, in contrast to synthetic PHGs, the biodegradation of hydrogels of natural origin is not questioned. The biodegradation of hydrogels of mixed nature depends on the ratio of natural and synthetic components, and the first stage of this process is the decomposition of such a polymer into shorter units. Moreover, both the ability to swell and retain water, and the rate of biodegradation depend on the type of cross-linking agent. For example, in the work of P. Jungsinyatam et al. [69] it was shown that glutaraldehyde, but not ethylene glycol dimethacrylate or N,N′-methylenebisacrylamide, can be considered the most preferred cross-linking agent for the synthesis PHG from cassava starch, acrylic acid, natural rubber and vinyl alcohol, which provides the best biodegradability of this PHG.

Hydrogels with biologically active fillers. The problem of low efficiency of fertilizer use can be solved by creating a new technology for their controlled release, which will increase the efficiency of consumption of nitrogen, phosphorus, potassium and other elements by plants and reduce environmental pollution. In this case, fertilizers are encapsulated in shells made of polymeric materials and are released during their gradual destruction (Fig. 2).

There are two methods for loading hydrogels with nutrients: during synthesis of the cross-linked copolymer (in situ loading) and after the hydrogel is prepared (ex situ loading) [31]. Ammonium nitrate, ammonium phosphate, and potassium chloride included in the hydrogel matrix are available to plants for a much longer time than when these minerals are directly added to soils [70]. Urea is a commonly used nitrogen fertilizer, but has rather low efficiency due to its high rate of decomposition and volatilization. One solution to this problem may be the

gradual release of urea into the soil from hydrogels, in which case two goals achieved are water retention and supply of nitrogen fertilizer to crops.

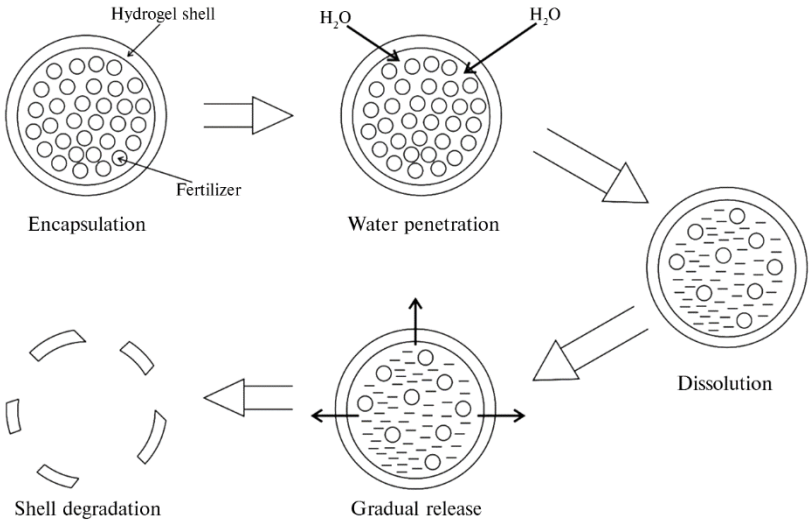

Fig. 2. The mechanism of release of compounds encapsulated in a polymer hydrogel.

Fertilizers that combine water holding capacity, sustained release, and safety for rhizosphere bacteria have been developed based on polyacrylonitrile and acrylic acid hydrogels. Urea granules were coated with oleic acid, soybean oil, and linseed oil, and the outer shell was acrylonitrile, polymerized alone or in combination with acrylic acid [71].

New composite hydrogels were synthesized from sodium alginate, cellulose nanofibers and polyvinyl alcohol with the addition of fertilizer containing nitrogen, phosphorus and potassium. Such hydrogels had good swelling ability in water and slow release of minerals [72]. Soil conditioners based on whey alginic acid hydrogel have been developed for moisture retention and sustained release of urea [73].

Nanoparticles made from biopolymers can be used for the controlled release of mineral fertilizers and pesticides. Nanosized carriers can be used to deliver pesticides with a controlled and gradual release profile, thereby achieving the goals of so-called precision agriculture, which aims to deliver a specific substance directly to the plant without causing water and soil pollution [74]. A naturally occurring polymer, chitosan can be used in agriculture as a matrix for encapsulating plant nutrients. Thus, it was demonstrated that wheat growth was accelerated with an increase in yield and a reduction in the life cycle from 170 to 130 days when using chitosan nanoparticles with nitrogen, phosphorus and potassium, which were applied to the surface of the leaves and penetrated into the stomata when absorbing gas. In this case, direct interaction of these nanoparticles with soil was excluded [75].

By controlling the release of pesticides from the hydrogel matrix, the efficiency of their use can be increased [76]. Composite hydrogels based on alginate and acrylamide have been developed for controlled release of glyphosate [77], acrylic nanocomposite hydrogels of starch with montmorillonite and chlorpyrifos [78], and hydrogels consisting of calcium alginate, attapulgite, polydopamine with pH-sensitive controlled release of this insecticide [79]. Starch-based PHG was synthesized for the controlled release of the fungicide carbendazim [80], as well as CMC polymers containing the insecticide thiamethoxam cross-linked with boric acid [81] and hydrogel composites obtained by cross-linking CMC with citric acid in the presence of bentonite [82].

In the process of obtaining polyacrylamide and polyacrylate hydrogels, various fillers can be used. Thus, the biotechnological synthesis of acrylamide from acrylonitrile is carried out with a biocatalyst based on nitrile hydrolyzing bacteria [83], and the waste of this process is the spent sludge of the biocatalyst. When using biocatalyst sludge as a filler, several goals can be achieved, including reducing the cost of the water-retaining preparation, recycling biotechnological production waste, and introducing an additional organic food source for soil bacteria [16, 84].

Hydrogels as carriers of bacterial preparations (biofertilizers). The use of biofertilizers is emerging as an alternative practice that promotes sustainable agriculture and restoration of degraded soils. Biofertilizers based on living microorganisms are applied to seeds or soil for subsequent colonization of the rhizosphere. To immobilize bacteria that stimulate plant growth, inert carriers are required that will protect microorganisms from adverse environmental influences, ensure their gradual release and the possibility of long-term storage of such a preparation without loss of viability of immobilized microorganisms.

The most common way to isolate microorganisms from the environment is their encapsulation. Microorganisms are coated with a semi-permeable polymer through which they are released under certain conditions. An example is the development of a biodegradable and biocompatible hydrogel with ionic cross-links based on a mixture of chitosan and starch for the immobilization of bacteria which attach to the outer surface of the granules and the walls of the channels of this polycomplex and form agglomerates and multilayer biofilms. The hydrogel was prepared as follows: the tripolyphosphate anion interacted with the protonated amino groups of chitosan, which was then mixed with starch, pregelatinized by heating [85).

Calcium alginate has been proposed as a matrix for encapsulating azospirillum. Such immobilized bacterial preparations retained proliferative function and metabolic activity [86]. A composite of polybutylene succinate grafted with acrylic acid and starch was proposed, containing phosphate and an encapsulated bacterial fertilizer based on the phosphate-mobilizing bacterium *Bacillus* sp. PG01. Starch introduced into the matrix improved its biodegradability. The release of bacteria into the soil occurred during the destruction of the composite, so the rate of this process and the amount of released bacterial fertilizer can be adjusted by changing the ratio of starch and polybutylene succinate in the hydrogel composition [87].

Soil microbiota significantly affects plant growth, their productivity and resistance to stress, so a natural question arises about the impact of GHGs of various origins on environment-forming soil microorganisms. Synthetic polyacrylate hydrogels have been shown to have no negative effects on microbiota [84]. The addition of rice straw-based hydrogels to the soil improved the microbial composition of the soil, with an increase in the proportion of *Azotobacter* spp., as well as phosphate-mobilizing bacteria, fungi, and actinomycetes [88], but the acrylic-based polymer did not affect the content of actinomycetes and fungi in the soil [89]. It has also been shown that the addition of alginate-based PHG has a positive effect on soil microbiota: the addition of this polymer in an amount of 5% led to an increase in the abundance of fungi, bacteria and actinomycetes, respectively, by 28, 30 and 38% [32].

The influence of hydrogels on the growth of agricultural crops and ornamental plants. The table shows the effect of some hydrogels used as water-retaining agents on plant growth, crop survival and productivity.

Effect of polymer hydrogels (PHGs) on plant growth and development

Hydrogel	Plant	Observed effect	References
(RITEK-ENPC LLC, Russia), copolymer of acrylamide and potassium acrylate Aquasorb (SNF s.a.s., France)	Spring wheat (Triticum aestivum L.), Esther variety	A significant increase in grain yield up to 35.70 c/ha when using the gel together with the application of nitrogen fertilizer	[90]
PHG granulated (composition and manufacturer not specified)	Winter wheat (*Triticum aestivum* L.), variety Donskoy Surprise	When PHG was applied at a dose of 80 kg/ha, the yield was 3.047-3.222 t/ha (an increase of 0.210-0.280 t/ha relative to the control), the wet gluten content increased by 0.8-1.0%	[91]
Polyacrylamide Praestol 650 (WaterChem LLC, Russia)	Winter wheat (*Triticum aestivum* L.), variety Bezenchukskaya 308; spring barley (*Hordeum vulgare* L.), variety Nutans 553; peas (*Pisum* L.), variety Flagman 12	Increase in yield for winter wheat is 0.24-0.72 t/ha, spring barley 0.14-0.41 t/ha, peas 0.02-0.07 t/ha. In combination with manure and mineral fertilizers, the increase in yield for wheat is 1.30-1.56 t/ha, barley 1.20-1.29 t/ha, peas 0.19-0.23 t/ha	[92]
Ritin-10 (RITEK-ENPC LLC, Russia)	Winter wheat (*Triticum aestivum* L.), variety Bagheera	Increase in crop productivity with the combined use of hydrogel (200-300 kg/ha) and fertilizers by 8.1-17.4 c/ha (31.9-68.6%); increase in raw gluten content by 0.2-3.6%	[93]
PHG (composition and manufacturer not specified)	Winter wheat (*Triticum aestivum* L.), variety Bagheera	In the 4th year after the use of PHG (400 kg/ha), the yield increased by 6.1-6.5 c/ha	[94]
PHG (composition and manufacturer not specified)	Winter wheat (*Triticum aestivum* L.), variety Bagheera	In the 3rd year after applying PHG (100-400 kg/ha), the yield increased by 4.0-24.7 c/ha (8.8-44.0%)	[95]
Pusa Hydrogel (India) based on cellulose and anionic polyacrylate	Wheat (*Triticum aestivum* L.),	Increased growth rate	[114]
PHG based on acrylamide and acrylates, 0.1-0.3% (synthesized in the laboratory by polymerization of N,N-methyl-bis-acrylamide and a mixture of Na and K salts of acrylic acid)	Common barley (*Hordeum vulgare* L.)	Increasing the rate of seed germination	[96]
Lignin hydrogel (synthesized in the laboratory from alkali lignin and polyethylene glycol diglycidyl ether)	Corn (*Zea mays* L.)	Increased plant height, biomass and phosphorus content using hydrogel under drought conditions	[97]
Hydrogel ша carbamate starch phosphate with urea (synthesized in the laboratory)	Corn (*Zea mays* L.)	Increase in the number of leaves, average leaf length and stem width of seedlings	[98]
Cross linked potassium polyacrylate hydrogel (manufacturer not specified)	Corn (*Zea mays* L.)	Increase in plant height by 26.3% on loamy soil with the application of 0.5% PHG, more than 2 times on sandy soil with the application of 1% PHG	[99]
Acrylamide polymer water-absorbing AK-639 series (Akripol LLC, Russia	Carrot (*Daucus carota* L.)	Increased field germination by 33%, plant density by 24%, yield by 32%, and marketable root crop yield by 12%	[100]
Ritin-10 (RITEK-ENPC LLC, Russia)	Carrot (*Daucus carota* L.), variety Samson (Nantskaya type)	When seeds are inlaid with gel, the increase in yield relative to the control is 93.7 c/ha	[101]
Water-absorbing acrylamide polymer series AK-639, grade B-415K (Akripol LLC, Russia)	Carrot (*Daucus carota* L.), beet (*Beta vulgaris* L.)	Increase in field germination of carrots by more than 3 times, yield - up to 90.5 t/ha, marketability of root crops - up to 84.3% (control - 57.2 t/ha and 77.1%, respectively). Beet yield - 55.4 t/ha with marketability of root crops 87.5% (control - 35.6 t/ha and 75.0%)	[102]
PHG (composition and manufacturer not specified)	Potato (*Solanum tuberosum* L.), varieties Zhukovskii rannii, Udacha abd Nevskii	Increase in the yield of the Zhukovskii rannii variety to 31.0-33.0 t/ha (by 3.6-11.2% of the control), of the Udacha variety to 33.4-36.9 t/ha (by 13.2-25.2%), varieties Nevskii up to 28.5-31.6 t/ha (by 9.9-22.0%)	[103]
Ritin-10 (RITEK-ENPC LLC, Russia)	White cabbage (*Brassica oleracea* L.), variety Kuizor	When treating the roots with gel, the increase in yield is 20.2 c/ha vs. control, when adding the gel to the soil is 6.0 c/ha	[101]
Cellulose-based PHG (synthesized in the laboratory)	Cucumber (*Cucumis sativus* L.)	Increase in plant growth rate and height, leaf fresh weight and area	[104]

Continued Table

PHG based on chiosan with copper nanoparticles (synthesized in pilot plant of the Research Center for Applied Chemistry, Mexico)	Tomato (*Lycopersicon esculentum* L.)	Increased yield and improved taste	[105]
Polyurethane hydrogel (synthesized in the laboratory)	Tomato (*Lycopersicon esculentum* L.)	Increase in plant height by the 90th day of the growing season in relation to the control (240 cm): 300 cm for 1-2% PHG, 505 cm for PHG with fertilizer	[106]
Polyacrylamide gel Acrylex P-150 (JSC VECTON, Russia)	Radish (*Raphanus sativus* var. radicula Pers.)	Seed germination under irrigation (light chestnut soil) and the use of PHG is 82.5% (control 45%), an increase in the content of organic carbon in rain-fed aquaculture, there is no deformation of the root crop in the PHG variant with irrigation. Germination of seeds with PHG on the solonchak is 90% (control 5%), on the solonetz 50% (control 0)	[107, 108]
PHG based on serum, cellulose derivatives and polylactid (synthesized in the laboratory)	Radish (*Raphanus sativus* L.), common beans (*Phaseolus vulgaris* L.)	Increase in growth rate and survival rate by 20% when applying 1-2% PHG under drought conditions compared to control	[109]
PHG based cellulose (synthesized in the laboratory)	Radish (*Raphanus sativus* L.)	Increasing the rate of seed germination	[104]
Stockosorb® («Evonik Industries AG», Germay)	Chickpeas (*Cicer arietinum* L.)	No effect on yield found	[116]
PHG (composition and manufacturer not specified)	Chickpeas (*Cicer arietinum* L.)	Increasing the yield of peas up to 1555 kg/ha (control 1306 kg/ha), straw up to 2053 kg/ha (control 1593 kg/ha) when applying 10 kg/ha PHG	[117]
Agarose hydrogel with selenium (synthesized in the laboratory)	Mung beans (*Vigna radiata* L.)	Obtaining plants enriched with selenium	[113]
Pusa hydrogel (India)	Senna alexandria (*Cassia angustifolia* Vahl.)	Increased yield of leaves and pods (2324.7 and 675.7 kg/ha, respectively) with a hydrogel dose of 3 kg/ha compared to the control (1611.6 and 433.5 kg/ha)	[115]
Alginate (synthesized in the laboratory)	Lettuce (*Lactuca sativa* L.)	Increased biomass	[32]
Ritin-10 (RITEK-ENPC LLC, Russia)	Oilseed radish (*Raphanus sativus* L. var. Oleifera Metzg.), variety Tambovchanka	Yield increase by 15-27% with 200 and 300 kg/ha hydrogel	[110]
Ritin-10 (RITEK-ENPC LLC, Russia) and V415-K (Akripol LLC, Russia)	Perennial herbs	Increase in hay yield with Ritin-10 (200 kg/ha) by 1.2 t/ha, with B-415K (300 kg/ha) by 2.9 t/ha	[111]
Water-absorbing polymer PR3005 (SNF Holding Company, France)	Rosella (*Hibiscus sabdariffa* L.)	Increase in chlorophyll content index, leaf area, number of calyxes under drought conditions	[118]
Acrylic acid polymer Aquasin (Tampomechanika-Moscow LLC, Russia)	Pilea Cadieux (*Pilea cadierei*), striped tradescantia (*Tradescantia zebrina*)	When 5 g/kg PHG was added, the height of the Cadieu pilea increased more than 2 times vs. control, 4 g/kg PHG led to an increase in the number of shoots and leaves of tradescantia vs. control	[112]

Grain crops tested were spring [90] and winter wheat [91-95], common barley [96], corn [97-99]; vegetable crops were carrots [100-102], potatoes [103], white cabbage [101], cucumber [104], tomato [105, 106], radish [107, 108], radish [104, 109]. Among the PHGs, synthetic polymers based on acrylamide and acrylic acid [90, 92, 93, 96, 99-102, 107, 108, 110-112], polymers based on natural raw materials, the cellulose [104], chitosan [105], agarose [113], alginate [32], lignin [97], and semi-synthetic hydrogels [114] were tested. The vast majority of experiments have shown the positive effect of hydrogels on crop productivity [90-95, 100-103, 110, 111, 115], seed germination and plant growth [96, 97, 99, 102, 104, 106-108, 114], especially in drought conditions. It was shown that when there was a lack of moisture, PHG provided a significant increase in yield compared to the control (up to 70%).

So, the main property of polymer hydrogels is their ability to hold an

amount of water many times greater than their mass, which allows them to gradually release moisture to the plant. In addition, hydrogels are used as a depot of mineral fertilizers and pesticides (herbicides, insecticides, fungicides) with the possibility of their prolonged release. The use of GHGs in agricultural practice, despite their positive impact on the chemical and physical properties of the soil, the environment, soil water balance and productivity, is insufficient. This is mainly due to the cost of PHGs, which can be reduced by various additives, e.g., waste (for example, organic mass of spent biocatalyst from biotechnological production), added to the composition of hydrogels. Both synthetic and natural PHGs have their drawbacks: synthetic hydrogels decompose slowly due to their low biodegradability, while natural PHGs characterized by a high rate of biodegradation, do not have sufficient mechanical strength and moisture capacity. In this case, the solution to the problem may be the creation of GHGs of a mixed nature, containing synthetic and natural components. Hydrogels based on polymers and copolymers of acrylamide and acrylic acid are more promising as moisture-retaining and anti-erosion agents, and natural and semi-synthetic PHGs are more promising as carriers of fertilizers and pesticides. A fairly promising direction can be considered the introduction of bacterial preparations immobilized in hydrogel matrices into soils for the subsequent reproduction of bacteria in the soil, however, this is not sufficiently covered in the scientific literature and is still poorly implemented in practice.

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