

Hydrogel composites as eco-friendly materials for water storage

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Abstract:

Purpose: The persistent demographic increase means that the demand for water is constantly growing, but the availability of clean water is low. High temperatures and no precipitation result in hydrological droughts, which also have a severe impact on agriculture. The aim of the work was to investigate the potential use of superabsorbent hydrogels as water storage for irrigation of fields.

Methods: Hydrogels composed of natural polymeric materials can absorb water from atmospheric precipitation and release it gradually into the soil during drought.

Results: The use of biopolymer hydrogels reduces the frequency of field irrigation and increases the infiltration and water retention capacity of the soil.

Conclusions: The use of superabsorbent hydrogels in agriculture leads to the saving of water resources. According to the concept of sustainable development, biopolymer hydrogels that are environmentally friendly represent a large potential for use as a water storage in the agricultural sector.

Keywords: hydrogel, soil moisture, water, superabsorbent, drought

1. Introduction

The most drought-sensitive sector of the economy is agriculture. High temperatures and low soil moisture disturb the proper plants growth, leading to a reduction in the quantity and quality of crops. The problem also concerns water shortages on cultivated fields.

Direct application of water to the crop surface is a commonly used irrigation method, which unfortunately does not solve the problem of drought. As a result of evaporation or run-off, a significant amount of water is lost, plants take up too little water, which results in reduced yields. The use of sprinklers reduces wastage of water, but requires the purchase of expensive equipment that most farmers cannot afford. In the current ecological and economic situation in the world, the demand for water is constantly growing, but the availability of clean water is still decreasing. The effect of hydrological drought on agriculture is a global problem and forces scientists to look for new solutions. One of the temporary solutions is the use of hydrogel materials with good water absorption and retention properties even at high temperatures [1].

Hydrogels have a positive effect on the physical properties of the soil - they increase the water retention capacity, increase infiltration and reduce the frequency of irrigation. So far, the most popular hydrogels used in the agricultural sector are crosslinked polyacrylates or polyacrylamides. Hydrogels consist of a network of polymer chains and the interior is filled with water. These structures can absorb water from rain and store it. The application of hydrogels in the soil causes that the water is gradually released into the soil and plant roots can absorb it slowly, thanks to which they satisfy needs in a longer time. The hydrogel dose must be adapted to the soil conditions. Hydrogels composed of synthetic polymers are not biodegradable, which adversely affects the environment. The use of natural polymers (agarose, alginate, chitosan) can solve the problem of degradation of hydrogel structures. Irrigation based on biopolymer hydrogels can be a technology that will overcome the crisis of hydrological drought [2].

2. Drought and its impact on agriculture

We do not currently have a good definition of drought. Numerous definitions define only selected features that scientists consider most relevant to the description of the process. In many cases, these are simplified definitions, while the concept of drought should include both physical and social measures that have an impact on locally and regionally occurring phenomena.

With the phenomenon of drought, occurring permanently or periodically, we are dealing almost anywhere on earth. It is associated with long-term reduction of the balance between the average amount of precipitation and the evaporation of water in the area. However, this is not the only parameter that should be considered, especially in more dry areas. It is difficult to determine how hard the drought process is. This depends not only on the duration of the drought (which is possible to estimate after its end), intensity, geographic range and the requirements posed by human duality. The features of drought and its consequences can often have an impact on society, the economy and the environment. All these parameters make it difficult to determine the effect of a long-term drought on the area [3].

Drought causes a decrease in drinking water resources, an increase the risk of fires and dryness of the soil, which causes the destruction of crops. The persistent lack of precipitation seriously disturbs hydrological conditions. The first stage of the phenomenon is atmospheric drought. The long-term predominance of the amount of evaporating water over the amount of water supplied from the atmosphere results in the appearance of soil drought. In the last stage there are drops in water levels and flows in rivers, and even drying of smaller water reservoirs (hydrological drought) [4].

The hydrological drought is a serious threat to the ecosystem and society, which is associated with desertification and water shortages in many regions of the world. The development of hydrological drought is influenced by the climate occurring in a given area (solid climate and climate with strong seasonality). In regions with relatively constant weather conditions, drought occurs when rainfall is below normal. In contrast, the seasonal climate is characterized by summer and winter drought. Drought determines the lack of rainfall in the wet season. It occurs on the savannah, monsoonal and Mediterranean climate [5].

The definition of agricultural drought combines features of the meteorological drought feature (associated with a reduced amount of rainfall, and thus a reduction in soil moisture) with impacts on agriculture. The demand for plants for water varies and depends on the crops used and latitude. Agricultural drought takes into account the susceptibility of crops at different stages of crop development to negative drought factors, for example reduced soil moisture at the early stage of crop development will be more important to plant development than water shortage and harvest. A lack of humidity during the development of crops may result in a decrease in productivity. [6].

3. Hydrogels for water storage

3.1. Hydrogels

Hydrogels have the ability to absorb and store very large amounts of liquid in relation to their mass, which significantly increase their volume and do not undergo the process of dissolution. In dry environment, water can be released slowly, from this structure. Hydrogels are polymers hydrophilic macromolecular compounds that form a three-dimensional network. They have become more and more popular in medicine as drug delivery systems and in agriculture as carriers of nutrients for plants.

Hydrogels in the dry state are in the form of rolled up polymer bundles, which under the influence of water undergo gradual relaxation and elongation. The absorption process is completed, the hydrogel reaches maximum swelling and cannot take up more water.

The properties of hydrogels depend on their structure, degree of crosslinking, but also on the content of water and its state. Hydrogels can be classified on various bases, which are shown in Fig. 1.

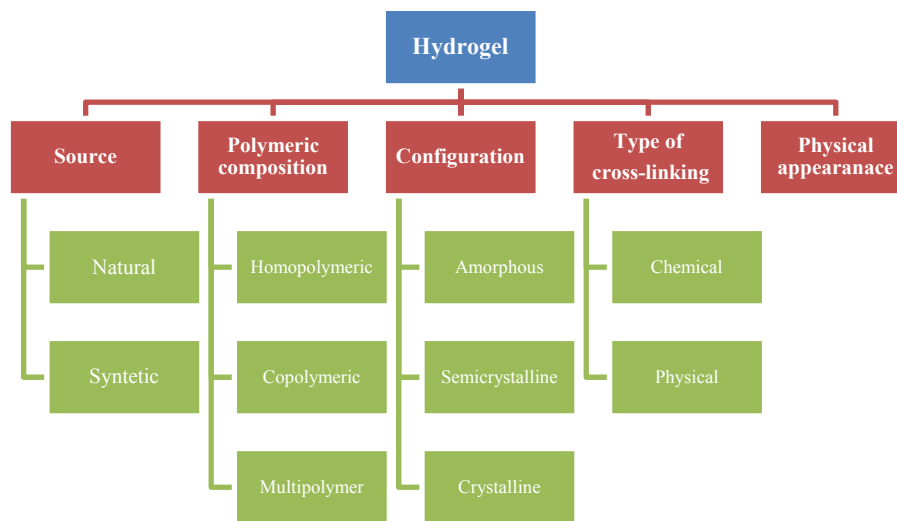


Fig. 1 Classification of hydrogels

A very important aspect in the classification of hydrogels is their origin. There are two types of polymers: synthetic and natural. For reasons of environmental protection, more attention is focused on biodegradable polymers (of natural origin). Examples of natural polymers are shown in Table 1.

Tab. 1. Examples of natural polymers.

Polymer	Functional Group	Gelations
<i>Gelatin</i>	- COOH, - NH ₂ , - OH	Ionic crosslinking; Chemical crosslinking;
<i>Alginate</i>	- COOH, - OH	Ionic crosslinking; Chemical crosslinking;
<i>Carboxymethyl cellulose</i>	- COOH, - OH	Ionic crosslinking; Chemical crosslinking
<i>Chitosan</i>	- NH ₂ , - OH	Ionic crosslinking; Chemical crosslinking;
<i>Fibrin</i>		Assembling and covalently crosslinking of fibril from thrombin cleavage of fibrynogen;
<i>Silk fibroin</i>	- COOH, - NH ₂	Sol-gel transition at presence of acid and ions;
<i>Agarose</i>	- OH	Gelation during cooling due to coil helix transition;

3.2. Mechanism of water absorption and release

The process of diffusion of water from polymer capsules takes place in several stages. Water from rainfall present in the soil solution migrates inside to the hydrogel (1). The stored water causes an increase in pressure inside the capsule (2) causing gradual release of water into the soil (3). The thickness and material of the polymer coating plays a very important role in the controlled release of water [7].

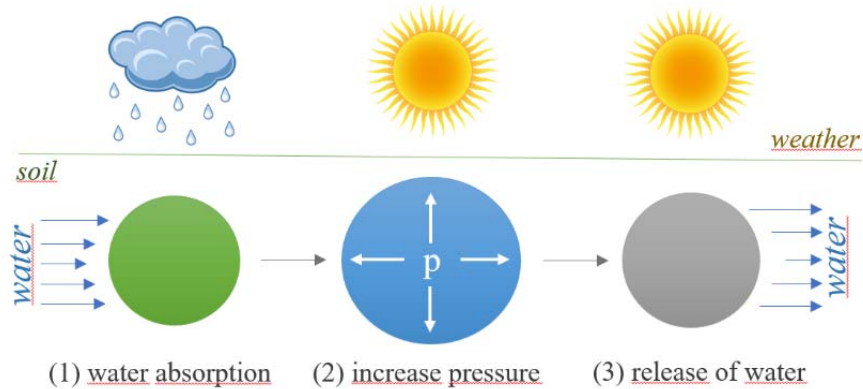


Fig. 2 Diagram absorption and release of water using a biocapsule.

From practical point of view is necessary to acquire model to describe water absorption/release rates from/to the capsules. Due to high water retention rate and polymers networks is common to approximate hydrogel as organic tissue and use models usually common in drug releasing experiments for process design.

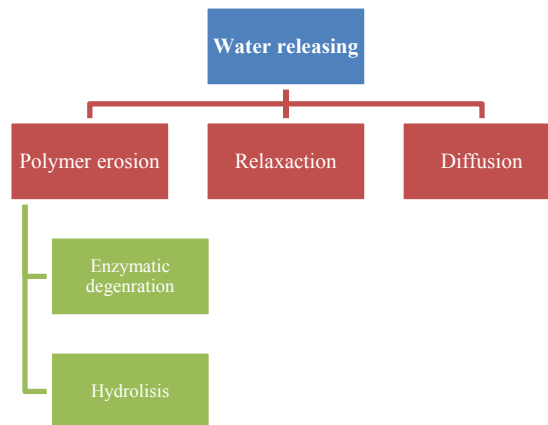


Fig. 3 Different modes of water releasing form hydrogels capsules

Most of mathematical models are relay on ideal condition and do not take polymer degeneration into assumption. Those group may divide into two categories: diffusion based and combination of relaxation and diffusion [8]. In 1961 Higuchi [9] proposed theoretical model based on assumption that: water diffusion has one dimension and has constant rate, matrix swelling is negligible, water particles are smaller than hydrogel thickens and perfect sink conditions are achieved in environment. This model is represented by equation:

$$Q = D(2C - 2C_s)C_s \cdot t \quad (1)$$

where: Q-water released [mass/time/area], C-initial water concentration, D – diffusion constant, C_s –water solubility in hydrogel media. This relation is based on the Fick's law and is time dependent.

It may be used for swelling as well as releasing water kinetics model [10].

Korsmeyer – Peppas semi-empirical model [11] is expressed by equation:

$$Q = at^n \quad (2)$$

where: a - is a constant depended by geometric and structure of hydrogel form, n – releasing exponent. The power of n determinate the type of water transport mechanic. Unlike to the Higuchi, this model take into consideration the polymer relaxation phenomena. The values of n determine water transport mechanism: 0.5 – Fick’s diffusion, $0.5 < n < 1$ – non Fick’s diffusion, 1- case II transport, values higher than 1 - super case II transport. This kind of approximation is often used for describing water releasing from several different hydrogel form.

Weibull model and their adaptation to the swelling/releasing processes [12] can be applied to all kind of dissolution curves. This is clearly empirical model and do not consist on any kinetic correlation. The obtained relation:

$$m = 1 = \exp - (T - T_i)^b a \quad (3)$$

where: a -process scale dependent parameter, T_i – lag time before process start, b – describes shape of curve progression, m - amount of water released in the function of time.

The main limitation of this model is connected with the issue of establishing in vivo/vitro correlation. Each of this model as well as other not mentioned in this has own limitation and is complicate to choose one which adjust the most in every case.

3.3. Biopolymer superabsorbents

Most of the materials available on the market are based on acrylates (synthetic polymers). Due to ecological aspects, hydrogels produced from natural polymers are more interested. [2] in their work the possibility of using superabsorbent cellulose-based hydrogels as a way to retain water in the soil was presented. Capsules showed the ability to absorb water up to 48%, and the soil moisture increased by 400%. The use of this type of hydrogel capsules would allow to minimize the losses associated with the cultivation of plants in countries struggling with drought.

Starch-graft-polymers is a wide group of superabsorbent with limited biodegradability due to presence of a non-biodegradable part of polymers [13] especially witch cross linked phosphoryl chloride in which can be included: starch-g-polystyrene, starch-g-polyvinyl alcohol, starch-g-methacrylonitrile, starch-g-acrylonitrile an so on. The most important issue of connected with preparation of those hydrogels are solubility of starch [14]. To overcome that problem many method was developed

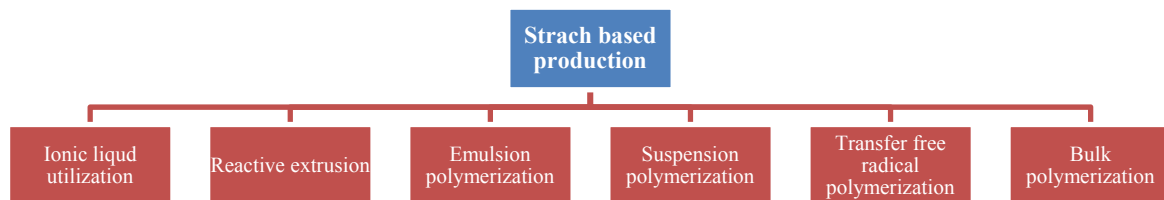


Fig. 4 Methods for starch based capsules production

In basic native form starch do not possess thermal and mechanical properties required to formulation stable capsules. Copolymerization with polymers chain and graft increasing values of that parameters [15].

In this paper capsules based on polysaccharides (alginate/carboxymethyl cellulose) were produced as superabsorbents for water storage.

4. Conclusions

In recent years, many studies have been carried out on the use of hydrogel composites in various applications. One of the most important properties of hydrogels is swelling in the aquatic environment and the possibility of its long-term storage. Currently, there is a drought problem in the world, which also affects the area of agriculture to a large extent. Polymers with the properties of storage and controlled release of water are a solution to this problem. Superabsorbents consisting of synthetic polymers are very well known, however they pose a threat to the environment, due to the lack of biodegradability. The alternative is a natural polymers, such as alginate or carboxymethylcellulose. Biodegradable hydrogels have great potential in application as superabsorbents in the agricultural sector.

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