






# The benefits of synthetic or natural hydrogels application in agriculture: An overview article

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**Abstract:** In recent years, a growing problem of water deficit has been observed, which is particularly acute for agriculture. To alleviate the effects of drought, hydrogel soil additives – superabsorbent polymers (SAPs) – can be helpful.

The primary objective of this article was to present a comparison of the advantages resulting from the application of synthetic or natural hydrogels in agriculture. The analysis of the subject was carried out based on 129 articles published between 1992 and 2020. In the article, the advantages of the application of hydrogel products in order to improve soil quality, and crop growth.

Both kinds of soil amendments (synthetic and natural) similarly improve the yield of crops. In the case of natural origin polymers, a lower cost of preparation and a shorter time of biodegradation are indicated as the main advantage in comparison to synthetic polymers, and greater security for the environment.

**Keywords:** biopolymers, hydrogels, infiltration, polyacrylamide, polyacrylic polymers, superabsorbent polymers (SAPs), surface runoff

## INTRODUCTION

Agriculture is one of the largest and most important branches of industry that produces food. Proper soil irrigation and its good condition are key factors in ensuring adequate yields and food production at the required level. The agricultural sector, as the largest user of water resources, is the most vulnerable to the effects of drought occurring more often and long-lasting [DAR *et al.* 2017; NEETHU *et al.* 2018; TADESSE *et al.* 2020; WALLACE 2000]. It is estimated that agriculture is responsible for 75% of current water use by humans [WALLACE 2000]. At the same time, on average 63% of water supplied to agricultural areas is lost as a result of evaporation and runoff [BAIAMONTE *et al.* 2015].

The water demand of plants should be satisfied by rainfall/irrigation and by water stored in the soil profile [HARISUSENO 2020; KOPACZ *et al.* 2018; KOWALCZYK *et al.* 2016; XU *et al.* 2015; ZUBALA, PATRO 2016]. Unfortunately, extended periods of drought deepen the water deficit, which adversely influences plant metabolism, including the photosynthesis process and the biochemical activity

of chloroplasts [LAWLOR 2002]. The lack of moisture in the root region often causes premature leaf fall, lowering the chlorophyll content and seed yield, as well as worse fruiting and flowering of plants [NEETHU *et al.* 2018]. The water deficiency leads to lower plant yields than under optimal conditions [BATOOL *et al.* 2015; NEETHU *et al.* 2018].

In the face of climate change and forecasts of an increase in food demand, predicted in the next 50 years, it is imperative to apply measures that will provide plants with access to water, even during periods of prolonged drought [ABOBATTA 2018; AGEGNEHUA *et al.* 2016; BAIAMONTE *et al.* 2015; NEETHU *et al.* 2018; SENNA, BOTARO 2017].

According to some scientists, an increase of water amount in the soil, which is available to plants (the so-called green water), directly influences the yields to increase per unit area, thus increasing food production [SPOSITO 2013]. Therefore, in order to reduce water losses, it is advisable to use appropriate amendments that help to retain water in the soil profile during periods of irrigation or rainfall, and gradually release water

in conditions of its deficiency [BUCHMANN *et al.* 2015; SOUZA *et al.* 2016; XU *et al.* 2015].

Such additives are hydrogels – superabsorbent polymers (SAPs). In their crosslinked structure, they can store water in an amount much greater than the volume of the dry hydrogel [NEETHU *et al.* 2018]. Their specific properties cause that hydrogels can replace the use of typical, known organic additives, e.g. peat, straw, compost [AGEGNEHUA *et al.* 2016; CHACHA *et al.* 2019; EDEN *et al.* 2017; MAYNARD 2000].

The addition of hydrogels to soil results in an improvement of the soil structure and its physical properties, such as water retention, permeability, infiltration rate, drainage, and aeration. The abilities of hydrogels to retain water, mineral components, and soil aggregation are often used in areas with abundant extreme weather events or on slopes exposed to erosive processes [LEE *et al.* 2013; LU *et al.* 2018]. The use of hydrogels is particularly beneficial in dry climatic regions, as well as on sandy and strongly eroded soils [LEE *et al.* 2013; LU *et al.* 2018]. They are useful on light soils with low water retention, which are very sensitive to lack of rainfall [KULIKOWSKI *et al.* 2018].

Additionally, SAPs improve substrate aggregation, therefore they counter water erosion caused by the detachment of soil particles resulting from rainfall and runoff [BELLOULA *et al.* 2020; BUCHMANN *et al.* 2015]. Their application in agriculture enables rapid planting and stabilisation of the area, therefore they are helpful in the reclamation of degraded areas [KULIKOWSKI *et al.* 2018; NEETHU *et al.* 2018; VUNDAVALLI *et al.* 2015].

The paper presents the methods of obtaining synthetic and natural polymers, as well as the mechanism of water accumulation and release. Selected benefits are presented, such as improvement of soil structure, reduction of erosion processes, infiltration improvement, and also increasing yield achieved after using both synthetic and natural polymer hydrogels. The results of research on the decomposition time and biodegradability of synthetic additives are discussed because the safety of using synthetic hydrogels has been arousing the most controversy.

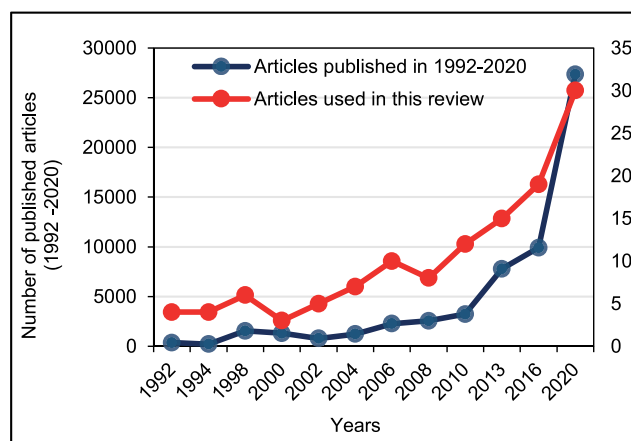
## STUDY METHODS FOR LITERATURE REVIEW

We used our own literature review protocol using the databases. We used the bases of Elsevier, SpringerLink, Scopus, Google Scholar, and appropriate keywords: hydrogels, superabsorbent polymers, soil water retention, infiltration, polysaccharides.

In recent years, there has been a growing interest in the use of SAPs in agricultural applications. This interest is reflected in the number of published articles. The number of publications found on the basis of Google Scholar, published in the years 1994–2020, is presented below (Fig. 1). These results were compared with the number of references chosen for the preparation of this review. The good agreement of both charts proves a reliable review of the literature.

All authors of the presented article took part in the preparation of the initial search of the literature. Literature materials were prepared during the three months of April–June, 2021.

For the search of the literature we used English keywords, but our literature analysis also included articles published in Polish with abstracts written in English. From these results, we selected 129 publications. The majority of them were concerned



**Fig. 1.** The comparison of the number of articles concerning the application of hydrogels in agriculture published in 1994–2020 with the number of publications used in the preparation of this article; source: own elaboration based on Google Scholar

with results of the use of hydrogels in agriculture (113 publications), while other publications describe the synthesis or mechanism of activity of chosen hydrogels (32 publications).

An interdisciplinary group consisting of a chemist, a specialist in environmental protection, a specialist in water and environmental engineering, and a hydrogeologist took part in the preparation of this review. Therefore, this article presents a chemical and a practical approach to the subject of hydrogels.

The overview contains chapters on the synthesis and mechanism of action of hydrogels because the literature describing the use of selected polymers often lacks such an explanation.

The application of synthetic and natural hydrogels for the limitation of erosion processes is presented in the following chapters and also in the form of Tables. The aim of this overview was to find the answer to questions concerned with the efficacy and security of SAPs applications in agriculture.

## RESULTS

### HYDROGEL PREPARATION

Hydrogels have the ability to absorb water in quantities exceeding their volume many times over. This property arises from the presence of hydrophilic functional groups attached to the polymeric backbone. Cross-links between network chains assure the resistance to dissolution [AHMED 2015].

Among the hydrogels, one can distinguish chemical or physical crosslinked hydrogels, both groups forming a three-dimensional crosslinked structure. In the case of physical crosslinked gels, the spatial structure is made of polymer chains held together by molecular interactions: Van der Waals forces, ionic interactions, hydrogen bonds [GUILHERME *et al.* 2015; KULIKOWSKI *et al.* 2018; TYLISZCZAK, PILICHOWSKI 2007]. Chemical crosslinked hydrogels are permanently crosslinked polymers whose chains are linked by covalent bonds [AHMED 2015; GUILHERME *et al.* 2015; SENNA, BOTARO 2017].

The most common components of synthetic hydrogels are vinyl monomers (1): acrylic acid, methacrylic acid and their derivatives, acrylamide and divinyl (2): N,N'-methylenebisacry-

lamide, ethylene glycol diacrylate, sodium divinylbenzenesulphonate, tetra- (hydroxymethyl) acetylene urea and allyl acrylate. Less frequently, ethylene glycol, aspartic acid, vinyl alcohol, maleic anhydride copolymers, N-vinylpyrrolidone and chemically modified copolymers based on starch and cellulose are used [BARTNIK 2008; KULIKOWSKI *et al.* 2018; TYLISZCZAK, PILICHOWSKI 2007].

Hydrogels are obtained using chemical methods by polymerising monomers (acrylamide, acrylic and methacrylic acid) or cross-linking polymers (polyvinyl alcohol, polyethylene oxide, poly-N-vinylpyrrolidone, polyacrylamide, as well as by radiation methods [BAI *et al.* 2015; MONTESANO *et al.* 2015; NEETHU *et al.* 2018; SENNA, BOTARO 2017; TYLISZCZAK, PILICHOWSKI 2007]. Redox polymerisation initiators and cross-linking agents are used in chemical cross-linking. An example of the chemical synthesis of a hydrogel can be the polymerisation of acrylic acid with N,N'-methylenebisacrylamide as a cross-linking agent in the presence of the polymerisation initiator – persulphate [GUILHERME *et al.* 2015; TYLISZCZAK, PILICHOWSKI 2007].

Another method of hydrogels obtaining is radiation cross-linking which occurs under the influence of high-energy or high-temperature radiation. The radiation of  $^{60}\text{Co}$  or  $^{137}\text{Cs}$  isotopes, as well as the stream of electrons generated in an accelerator are used most frequently. The linking of polymer chains occurs by creating permanent covalent bonds. Radiation cross-linking of hydroxyl groups in the presence of glutaraldehyde as a cross-linking agent is used to obtain a polyvinyl alcohol-based hydrogel [TYLISZCZAK, PILICHOWSKI 2007]. Polymerisation of acrylic acid with its water-soluble salts leads to the formation of sodium polyacrylate or potassium polyacrylate [KULIKOWSKI *et al.* 2018; NEETHU *et al.* 2018].

The most popular synthetic SAPs used in agriculture are ionic polymers (cationic, anionic, e.g. crosslinked polyacrylic acid, polymethacrylic acid and their salts), non-ionic polymers (e.g. crosslinked polyacrylamide), linear, non-crosslinked polyacrylamide [BARTNIK 2008; KULIKOWSKI *et al.* 2018; SOJKA *et al.* 2007].

An important group of polymers used in agriculture are hydrogels obtained on the basis of natural polymers. These polymers are an alternative to fully synthetic hydrogels. Usually, lower production costs and complete biodegradability are indicated as their advantages. However, natural polymers without earlier modification are not able to form hydrogels with good stability, which is crucial if they are to be used as carriers of nutrients. Therefore, the hydrogels from polysaccharides are prepared using a chemical (more often) or physical crosslinking methods [FAJARDO *et al.* 2013; GUILHERME *et al.* 2015; SANNINO *et al.* 2009; SANNINO, NICOLAIS 2005; YAN *et al.* 2009]. The following polysaccharides are used to obtain natural hydrogels: pectin, cashew gum, acacia, guar gum, starch, chitosan, chitin, cellulose, alginate, agarose, and proteins (collagen, gelatine) [ABDEL-RAOUF *et al.* 2018; BAI *et al.* 2015; DAS *et al.* 2020; DENG *et al.* 2015; GUILHERME *et al.* 2015; LEE *et al.* 2013; LU *et al.* 2018; NEETHU *et al.* 2018; SARMAH, KARAK 2020; THOMBARE *et al.* 2018].

Polysaccharides, such as pectin, cashew gum, Arabic gum, and starch were modified through vinyl groups incorporation into their structure. The chemical modification of cashew gum, pectin or starch was carried out using glycidyl methacrylate, in the presence of appropriate catalytic agents and with the use of organic solvents (e.g. dimethyl sulfoxide – DMSO). In the process of formation of vinylated Arabic gum, water was used as the

solvent and no additional catalytic agents were used [GUILHERME *et al.* 2015].

Another polysaccharide modification method is free-radical polymerisation. In this process, peroxides (such as potassium persulphate, ammonium persulphate) are used [GUILHERME *et al.* 2015; LEE *et al.* 2013; RABAT *et al.* 2016]. The polymerisation process starts from the decomposition of the peroxide agent and to the formation of radical ions in the polymer chain. The covalent crosslinks are formed by the reaction of vinyl monomers with the radical hydroxyl or carboxyl groups formed in the polysaccharide chain. Examples of free-radical modification of natural polymers are the crosslinking processes of peanut hull cellulose, kappa-carrageenan, sodium alginate, xanthan gum, chitosan [GUILHERME *et al.* 2015].

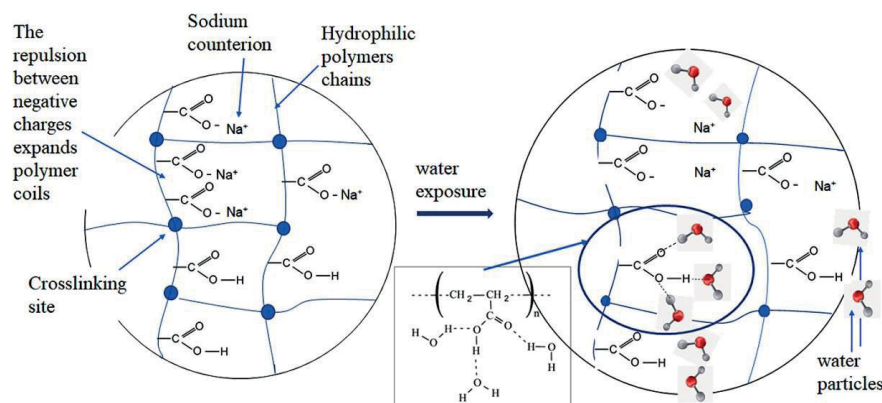
### MECHANISM OF HYDROGEL ACTIVITY

How do hydrogels work? How does water absorption/desorption occur in hydrogel structure? The water absorption process can be described in several stages. The ability of hydrogels to absorb water is related to their structure. When hydrogel is exposed to an aqueous solution, water molecules are attracted to the polymer chains across the gel surface [FENNEL, HUYGHE 2019]. Hydrogel functional groups, influenced by water, undergo solvation and then dissociation. In the case of presence of carboxyl groups (anionic groups), a negative charge accumulates on the polymer chains, causing the chains to repel and creating a space that enables further water absorption. At the same time, hydrogen bonds are formed between the oxygen of the carboxyl groups and the water protons, stabilising the swollen hydrogel structure (Fig. 2) [BAHRAM *et al.* 2016; BARTNIK 2008; BASHIR *et al.* 2020; KUMAR *et al.* 2018; LIWIŃSKA 2019].

Thus, when the hydrogel is introduced into water or a solute solution, anionic or cationic groups are formed in the polymer segments, which causes chains repulsion and stretching of the polymer. As a result, electrostatic repulsions among either uniformly charged regions of the polymer drive the diffusion process of the water or solute into the hydrogel network. The stretching of polymeric chains is counterbalanced by elastic retractive forces [GUILHERME *et al.* 2015].

Additionally, the swelling processes and water release are regulated by osmotic processes. In the course of the dissociation process of polymer's functional groups, the counter-ions of sodium are generated. These ions ensure the electrical neutrality of hydrogel and increase osmotic pressure in gel coils. Differences between osmotic pressure inside and outside the gel are caused by the difference between the concentration of counter-ions inside the gel (e.g.,  $\text{Na}^+$ ) and the concentration of an ionic compound in the external aqueous solution. Water moves across the semi-permeable gel boundary, but the flow direction depends on the osmotic pressure difference inside and outside the gel. Thus, the process of hydrogel swelling or shrinking is the result of the osmotic pressure difference [FENNEL, HUYGHE 2019; KUMAR *et al.* 2018].

The processes described above lead to the accumulation of large amounts of water in the polymer structure, significantly exceeding the molecular weight of the hydrogel. The hydrogel capacity (swelling degree) is a parameter expressed in grams of solution or water that has been absorbed by 1 g of dry polymer. The type of functional groups and the degree of cross-linking of the polymer affect the hydrogel capacity. The hydrogel swelling



**Fig. 2.** The scheme of structure of a superabsorbent polymer (sodium neutralised polyacrylate) on the left; the idea of creation of hydrogen bonds formed between the oxygen of the carboxyl groups and water protons; source: own elaboration based on: BARTNIK [2008], FENNEL and HUYGHE [2019], KUMAR *et al.* [2018]

degree will also depend on its degree of fragmentation and the type of substances contained in the absorbed solution [BASHIR *et al.* 2020; KUMAR *et al.* 2018; TYLISZCZAK, PILCHOWSKI 2007].

Greater numbers of hydrophilic groups in hydrogel polymeric structure aid the adsorption of greater water quantity. Comparative studies of potassium polyacrylate (Aquasorb) and acrylamide-acrylate copolymer (Aquaterra), with similar grain size, showed better water absorptivity of polyacrylate because of the greater numbers of hydrophilic groups in the case of polyacrylate [DĄBROWSKA, LEJCUŚ 2012].

The water absorbed by the hydrogel, called interstitial water or pore water, is contained between solid soil particles and held in these spaces by capillary forces; it possesses a specific pH and contains various ions. The presence of dissociated salts in the pore water, including calcium or magnesium carbonates responsible for water hardness, affects the hydrogel swelling degree. The presence of metal ions ( $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ) reduces the absorbency of hydrogels [LEJCUŚ *et al.* 2008]. When monovalent cations (sodium, ammonium) are present in water, the absorption capacity of acrylic hydrogels is reduced by about 65%. In the case of divalent (calcium, magnesium) or trivalent (iron) cations, the ability of water absorption is reduced by over 80% [DĄBROWSKA, LEJCUŚ 2012; KULIKOWSKI *et al.* 2018]. Non-ionic (polyacrylamide) hydrogels are less sensitive to an increase in the ionic strength of solutions and the cross-linking properties of metal ions [KULIKOWSKI *et al.* 2018].

The hydrogel's absorbency can also be modified depending on the pH of the soil. SAPs absorb water well in the range of  $\text{pH} = 4\text{--}11$ , while at  $\text{pH} = 3$  and below, the absorption significantly decreases and almost completely disappears at  $\text{pH} = 1.5$  [LEJCUŚ *et al.* 2008]. On the other hand, the research carried out on modified pectin indicated decreased water absorption with increasing pH. Hence, it was confirmed there is a pH range favourable for the storage of more water quantity by hydrogel [GUILHERME *et al.* 2009; 2015].

Hydrogels can absorb over 1000 g of water per 1 g of dry matter [BARTNIK 2008]. However, in agriculture, hydrogels whose swelling degree is at the range of 400–600  $\text{g}\cdot\text{g}^{-1}$  are used most often. Too high a swelling degree of hydrogel reduces its mechanical strength [KULIKOWSKI *et al.* 2018].

In order to improve the mechanical strength of hydrogels, nanofillers (nanowhiskers) made of cellulose or chitosan [RODRIGUES *et al.* 2014], as well as inorganic substances – kaolin

[WU *et al.* 2003], montmorillonite [LEE, YANG 2004], attapulgite clay [ZHANG *et al.* 2006] are used. These additives not only strengthen the structure of the polymers, but can also improve the swelling ratio and the swelling rate [GUILHERME *et al.* 2015].

An important parameter that informs about the availability of water enclosed in a hydrogel to plants is the osmotic potential of the water in the hydrogel. This parameter is expressed by analogy to the osmotic potential of soil water  $pF = \log F$ , where  $F$  (expressed in  $\text{cm H}_2\text{O}$  column) is a measure of soil suction. The  $F$ -value is the height of the water column that can be sustained by this force. The value of the suction power increases as the soil dries. In soil saturated with water  $pF = 0$ , in dried soil  $pF = 7$ . Plants are able to take up only a part of the water that is below  $pF = 4.2\text{--}4.5$ . This value coincides with the wilting point of most crops. The research on SAPs shows that the potential of water bound in SAPs that can be absorbed by plants is in the  $pF$  range of 2.0–4.2 [KULIKOWSKI *et al.* 2018].

The values of the water osmotic potential are measured using direct measurements carried out with the help of methods used in soil analysis and also on the basis of determination of the wilting point. Experiments show that the use of hydrogels increases the bioavailability of water for plants [KULIKOWSKI *et al.* 2018].

An undisputable advantage resulting from hydrogels application to the soil is the improvement of soil condition. Through repeated swelling and shrinkage processes, the hydrogel has a positive effect on the soil structure. These processes improve the infiltration rate, bulk density, and soil aeration [AL-HUMAIM 2005; BARTNIK 2008; DEMITRI *et al.* 2013; EL-ALSAYED, ISMAIL 2017; MONTESANO *et al.* 2015; SANNINO *et al.* 2009]. The addition of hydrogels to the soil promotes the growth of soil microcapillaries by mechanically blocking the bigger tubules in the soil. This limits evaporation, gravitational outflow of water and the loss of the nutrients dissolved in it [BARTNIK 2008; DEMITRI *et al.* 2013; KULIKOWSKI *et al.* 2018]. Thanks to these processes, water is retained in the soil for longer, and thus the moisture in the soil increases.

## EROSION PROCESSES LIMITATION THE USE OF SYNTHETIC POLYMERS

Soil susceptibility to erosion processes is conditioned by its properties, structure, the slope of the land, the intensity of rainfall, and the agricultural practices applied. Usually, leaching



processes are more intense in the mountains, where the slope of the terrain is higher [AGASSI, BEN-HUR 1992; LEE *et al.* 2011; POLYAKOV, LAL 2004]. Compared to non-eroded soils, eroded soils have a greater tendency to surface sealing, soil compaction, reduction of overall porosity and retention of useful water for plants, and water permeability deterioration [PALUSZEK 2001]. Soil sealing results in a slower infiltration rate, and thus a shorter water retention time and greater surface runoff [FOX, BRYAN 1999].

For the purpose of erosion prevention, remedial procedures are applied, e.g. those included in The Best Management Practices (BMP), such as mulches, vegetation buffer strips, contour farming, perennial plant, cultivation, grassland formation, no-till cultivation, cover crops [LEE *et al.* 2013]. Apart from these well-known procedures, also new ones are available now. Already in the 90s of the last century, attention was drawn to the benefits of using polymeric soil amendments. It was confirmed that hydrogels impact the formation of soil aggregates typical for a fertile soil. The changes in soil structure limit the infiltration rate, decrease the quantity of suspensions in soil leachate, and in effect reduce erosion [LEE *et al.* 2013; ORTS *et al.* 2007]. Polyacrylate and polyacrylamide hydrogels are the most popular synthetic polymers used towards the improvement of soil structure [ABU-ZREIG 2006; DĄBROWSKA, LEJCUŚ 2012; SOJKA *et al.* 1998a; SOJKA *et al.* 1998b]. Below, some examples of their application are presented.

The structure of soil aggregates and the rate of individual fractions characterise soil fertility. A fertile soil contains permanent aggregates with dimensions of 0.25–10 mm, especially aggregates at 1–5 mm are beneficial for plant growth. In strongly eroded soils, an increase of aggregates with dimensions above 10 mm and micro aggregates below 0.25 mm, arising from larger aggregates breakdown due to the action of water, is observed. Soils containing more aggregates with dimensions above 10 mm are characterised by a weaker water-resistance of aggregates, higher density, lower retention of water useful for plants, lower air permeability, and are more prone to erosion during intense rainfall. The application of polymer amendments allows an increase of the number of aggregates with dimensions between 0.25 and 10 mm [LOWERY *et al.* 1995; PALUSZEK 2001; 2010].

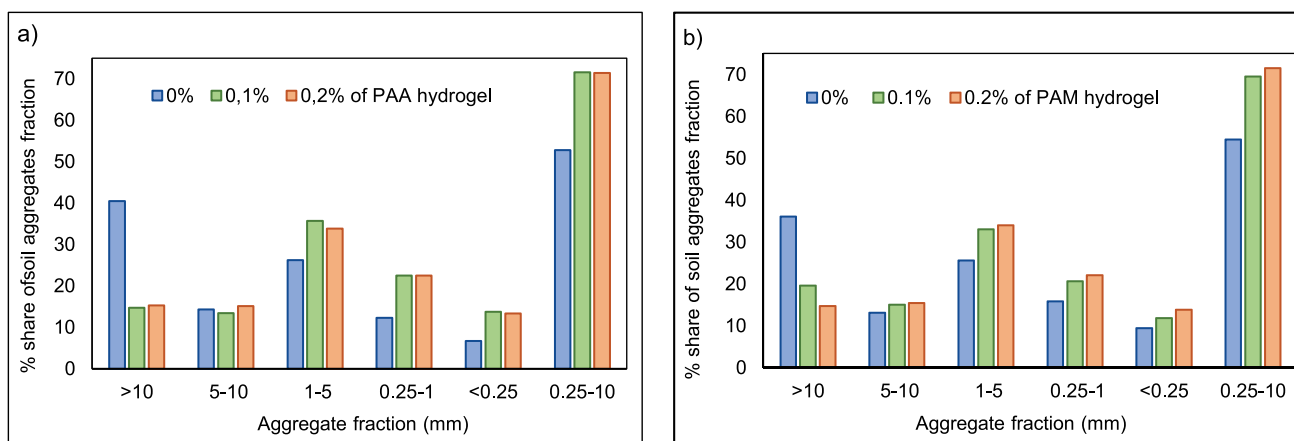
A commercially available anionic crosslinked polyacrylamide and potassium polyacrylate copolymer (the trade name Stockosorb) was tested in the experimental field of the Department of Soil and Plant Cultivation of the Academy of Agriculture in Poznań (Poland). The hydrogel was applied in two kinds of soil – a grey-brown podzolic soil (loamy sand) and a black earth (sandy loam). The polymer was added to the soil in four doses, as mixtures with soil, in the amounts of 0.033, 0.066, 0.132 and 0.264% of dry soil mass. The use of Stockosorb advantageously affected the breakdown of primary aggregates and the formation of secondary aggregates larger than 0.25 mm. The number of secondary aggregates increased by 6–12% as a result of static water action. Aggregates bigger than 0.25 mm were formed, within the range of 5–7%, along with an increase of the dose of the hydrogel. In both types of the tested soils, the result of secondary aggregation was the formation of soil aggregates with dimensions >0.25, 0.5, and 1 mm. 10–25% was the aggregate fraction with dimensions from 0.25 to 0.50 mm, 2–18% was the fraction with dimensions from 0.5 to 1.0 mm, the sum of aggregates above 0.25 mm was 37–39% [OWCZARZAK *et al.* 2006].

Another consequence of the aggregate structure changes was a decrease of soil bulk density, an increase of aggregates porosity, and the time of water translocation in aggregates decreased two- or three-fold. Maximal capillary capacity increased by 19% v/v in the loamy sand and by over 13% v/v in the sandy loam [OWCZARZAK *et al.* 2006]. The copolymer of polyacrylamide and polyacrylate (Stockosorb) was tested also in another study, where the dose of 0.5–1 g·kg<sup>-1</sup> resulted in beneficial changes in soil aggregates dimensions, but a weaker effect on the improvement of water-resistance of aggregates was noted [PALUSZEK, ŻEMBROWSKI 2006]. In subsequent studies, another commercially available sodium polyacrylate (Hidroplus) was used in doses of 0.5–1 g·kg<sup>-1</sup>, which significantly improved the water-resistance of soil aggregates [PALUSZEK, ŻEMBROWSKI 2007].

Interesting experiments were carried out on a private farm in Bogucin on the Nałęczowski Plateau, on loessal soils. The effect of two commercial hydrogels on the improvement of soil structure was tested. The granulometric analysis of the tested soil, treated in the first experiment, showed the following composition: 57.4–59.6% of the dust fraction, 40–42% of the floatable parts, including 15–17% of loam. In that experiment, polyacrylamide hydrogel (AgroAquaGel) was used. The addition of hydrogel into the soil, in the amount of 0.1% and 0.2%, indicated a positive effect on the reduction of aggregates with dimensions >10 mm. The lower dose of the hydrogel (1 g·kg<sup>-1</sup>) decreased this fraction by 0.165 kg·kg<sup>-1</sup>, while the higher dose (2 g·kg<sup>-1</sup>) – by 0.214 kg·kg<sup>-1</sup>. An increase in the number of aggregates with dimensions of 10–0.25 mm was observed, which is beneficial for improving soil fertility. The quantity of 5–10 mm aggregates increased by 0.019 kg·kg<sup>-1</sup> after the addition of 0.1% of hydrogel, and by 0.023 kg·kg<sup>-1</sup> after the 0.2% dose, respectively. In the group of aggregates with dimensions of 1–5 mm, their number increased by 0.074 and 0.084 kg·kg<sup>-1</sup>, while the number of aggregates with dimensions of 0.25–1.0 mm increased by 0.048 and 0.063 kg·kg<sup>-1</sup>. The number of waterproof aggregates increased significantly with the dose of 2 g·kg<sup>-1</sup> [PALUSZEK, ŻEMBROWSKI 2008].

The second experiment, using AgroAquaGel 420, was carried out also in Poznań, on a loess soil. A commercially available polymer-potassium polyacrylate (AgroAquaGel 420) was tested. According to granulometric analysis, researched soil consisted of clay dust, containing 0.4–0.6% of the sand fraction, 57.4–59.6% of the dust fraction, and 40–42% of floatable parts, including 15–17% of clay. The hydrogel was added at quantities of 1 g·kg<sup>-1</sup> and 2 g·kg<sup>-1</sup>, similarly to the experiments described above. The quantity of aggregates with diameters above 10 mm decreased by 0.258 kg·kg<sup>-1</sup> when the dose of 1 g·kg<sup>-1</sup> was used, and by 0.252 kg·kg<sup>-1</sup> when the 2 g·kg<sup>-1</sup> dose was applied. The content of aggregates with dimensions of 1–5 mm increased, on average, by 0.095–0.076 kg·kg<sup>-1</sup>, in the case aggregates of 0.25–1 mm by 0.102 kg·kg<sup>-1</sup> and in the case of micro-aggregates of <0.25 mm by 0.070–0.066 kg·kg<sup>-1</sup> [PALUSZEK 2010].

Based on the data from the above two experiments, the quantitative changes of aggregates in fractions, depending on the amount of polyacrylamide hydrogel (PAM) or polyacrylate hydrogel (PAA) applied, are presented graphically below (Fig. 3). The data analysis clearly shows the beneficial effect of both commercially available hydrogels on the formation of aggregates smaller than 10 mm (Fig. 3).



**Fig. 3.** The comparison of changes in the quantity of soil aggregates fractions after a) polyacrylate hydrogel (PAA), b) polyacrylamide hydrogel (PAM) application to loess soil; source: own elaboration based on literature data analysis PALUSZEK [2010] and PALUSZEK and ŻEMBROWSKI [2008]

The PAA dose of  $0.1 \text{ g}\cdot\text{kg}^{-1}$  was slightly more effective than the same dose of PAM. PAA added at  $1 \text{ g}\cdot\text{kg}^{-1}$  caused a decrease of aggregates quantity of  $>10 \text{ mm}$  by 25.8%, however, the same quantity of PAM added to soil reduced the content of those aggregates by 16.5%. Similarly, the addition of PAA at  $1 \text{ g}\cdot\text{kg}^{-1}$  caused an increase in aggregates of  $0.25\text{--}10 \text{ mm}$  by 18.4%, while the same dose of PAM – by 15%. In the experiment using PMA, the use of dose of 0.2% of dry soil mass was more effective. Simultaneously with the improvement of the aggregate composition, a significant increase of water-resistant aggregates with dimensions of  $0.25\text{--}10 \text{ mm}$ ,  $5\text{--}10 \text{ mm}$ ,  $1\text{--}5 \text{ mm}$  was observed [PALUSZEK 2010].

In the second year after the soil was enriched with a hydrogel, in both experiments, the effect of the hydrogel was smaller but still significant. PAM used in the amount of  $1 \text{ g}\cdot\text{kg}^{-1}$  significantly improved the content of air-dry aggregates with dimensions of  $0.25\text{--}1 \text{ mm}$ . However, PAM added at the rate of  $2 \text{ g}\cdot\text{kg}^{-1}$  operated more effectively than the lower dose, increasing the number of aggregates with dimensions of  $0.25\text{--}10 \text{ mm}$  and the content of water-resistant aggregates with dimensions of  $0.25\text{--}1 \text{ mm}$  [PALUSZEK, ŻEMBROWSKI 2008].

Comparative studies on the effect of crosslinked PAA and PAM hydrogels on soil conditions were carried out also by other researchers. Hydrogels were tested in silt loam or loam soils [ABEDI-KOUPAI *et al.* 2008; AGABA *et al.* 2010; LENTZ 2020].

The subject of a study carried out in Kimberly (USA) was to compare the effects of two polymers (of Stockosorb type), obtained on the base of polyacrylic acid and polyacrylamide, on the improvement of soil condition. One of the hydrogels was an anionic crosslinked acrylate-polyacrylamide copolymer (XPAM – Stockosorb Agro-S), and the second hydrogel was a crosslinked polyacrylic acid-potassium salt (XPAA – Stockosorb 660). The research allowed the assessment of the impact of one-time addition of the polymers (XPAM or XPAA) at the dose of 0.25 or 0.5% of dry weight ( $5.6$  or  $11.2 \text{ Mg}\cdot\text{ha}^{-1}$ ) to a degraded calcareous silt loam. Control samples included unamended degraded soil and non-degraded soil (topsoil). The best results of soil water retention and plant available water (PAW,  $\text{g water}\cdot\text{g}^{-1}$  dry soil) were observed when the 0.5% dose of the polyacrylamide copolymer was added. It turned out the XPAM increased soil PAW more effectively than the XPAA. The values of PAW for other

polymeric doses followed in the order:  $0.5\% \text{ XPAM} > 0.25\% \text{ XPAM} > \text{topsoil} > 0.5\% \text{ XPAA} > 0.25\% \text{ XPAA} > \text{control}$ . The PAW ratio, calculated as the quotient of PAW of treated soil and PAW of control, after the application of 0.5% w/w PAM or PAA, changed from 1.3 to 3.5 for PAA and from 1.4 to 3.2 for PAM. Presented results confirmed that the effectiveness of both polymers is similar [LENTZ 2020].

Another paper describes the application of two commercial preparations of PAM (hydrogels, PR3005A and Tarawat A100). The hydrogels were mixed with three soil textures, sandy loam, loamy, and clay, at doses in the range of  $2\text{--}8 \text{ g}\cdot\text{kg}^{-1}$ . Plant available water (PAW) increased 1.8-fold relative to the control in clay, and 2.2-fold in loamy and 3.2-fold in sandy loam soil, with hydrogel application of  $8 \text{ g}\cdot\text{kg}^{-1}$  [ABEDI-KOUPAI *et al.* 2008]. In other experiments, polyacrylate hydrogel was used in sand, loam, silt loam, sandy loam, and clay soils, at 0.2 and 0.4% w/w hydrogel. The 0.4% hydrogel amendment caused a significant increase of the PAW (3-fold in sand, 2-fold in silt loam, and 1-fold in sandy loam, loam, and clay soils), compared to the control [AGABA *et al.* 2010].

The comparison of properties of PAM and gypsum preparations (PG) is the following issue connected with anti-erosion treatment. The test of PMA and PG application towards the improvement of infiltration fared favourably for PAM. PAM was used as a solution (dose of  $7.5 \text{ kg}\cdot\text{ha}^{-1}$ ), PG (97% gypsum, 0.6%  $\text{P}_2\text{O}_5$ ) was mixed with soil (dose of  $7.5 \text{ Mg}\cdot\text{ha}^{-1}$ ). PAM addition introduced into the soil improved infiltration values: 1.5 times for the samples of clay loam, 1.4 times for the samples of sandy loam, and 1.4 times for the samples of loam. The infiltration values were 39–48% greater after the application of PAM, compared to control trials. Applications of PG also increased the infiltration values: 1.4 times, 1.3 times, and 1.3 times, respectively, for the samples of clay loam, sandy loam, and loam. The infiltration values were 28–38% greater after the addition of the gypsum preparation. In that study, PAM indicated better efficiency towards infiltration improvement compared to gypsum preparation [KARAOGLU, ACAR 2018].

The efficiency of the application of anionic polyacrylamide (PAM) and phosphogypsum (PG) towards reducing runoff and erosion was evaluated on a sandy loam under natural rainfall conditions. Total runoff and soil loss for the control, gypsum, and

PAM treatments were 146, 48, and 81 mm and 3.1, 2.6, and 2.5 Mg·ha<sup>-1</sup>, respectively. Runoff was reduced by 67% after gypsum application and by 44% when PAM was used. Soil loss decreased by 16% after gypsum use, and by 19% when PAM was used. Hence, it was demonstrated the PAM was efficient in order to limit soil loss [ZHANG *et al.* 1998].

The use of 20 kg·ha<sup>-1</sup> PAM with 10 Mg·ha<sup>-1</sup> phosphogypsum allows obtaining very good erosion protection results on steep slopes of 30 to 60% [AGASSI, BEN-HUR 1992]. It was confirmed that PAM, at a dose of 4 kg·ha<sup>-1</sup>, was sufficient to control soil loss on clay soils with a slope of 5–7.5% [SEPASKHAH, BAZRAFESHAN-JAHROMI 2006]. The use of PAM in the amount of 40 kg·ha<sup>-1</sup> on 40% slopes reduced soil erosion by up to 72% compared to soil without the addition of a hydrogel [LEE *et al.* 2011].

Hydrogel preparations were used also for the limitation of turbidity and leaching of soil particles from cultivated field or construction zone. PAM at doses of 5 kg·ha<sup>-1</sup> and 10 kg·ha<sup>-1</sup> was applied in order to limit turbidity in coarse-textured soils – siliceous sand containing 86% sand and 6% clay. It was confirmed the PAM with anionic charge was more effective than that with cationic or non-ionic charges. PAM with a high-density anionic charge was chosen for application. PAM at the rate of 10 kg·ha<sup>-1</sup> reduced the turbidity of water by 83% compared with the control. The split dose was more effective than a single application. The results indicated that the rate of 5 kg·ha<sup>-1</sup> PAM was as effective as the rate of 10 kg·ha<sup>-1</sup> in reducing turbidity. PAM was also used in gypsum combinations. The applied mixture reduced the turbidity by more than 99% compared with the control. The application of a mixture of PAM and gypsum allows using a smaller quantity of gypsum [SIVAPALAN 2002].

PMA-type hydrogels were used successfully to reduce the leaching of silt and clay-size particles from construction sites in the Pacific Northwest area, which is particularly exposed to heavy rains from October to April, leading to leaching of soil sediments and soil erosion. Sediment was seeping into surface waters in amounts exceeding the restrictive water-quality standards of Washington state. Standards provide that leaching water

discharges must not raise turbidity by more than 5 nephelometric turbidity units (NTUs) or 10% above background in lakes and streams with the highest-class cleanliness. The sedimentation processes limiting turbidity of leached water are often able to capture the fine silts and clay-size particles (5–10 µm) responsible for turbidity, therefore it is necessary (1) to emphasise the importance of erosion prevention and (2) – to implement improved sediment controls. It turned out that the wet application of PAM allowed an effective decrease of turbidity. The most effective PAM dosage was in the range of 40–80 mg·dm<sup>-3</sup>. In the case of wet application of PAM, the dose of 10 mg·dm<sup>-3</sup> was more effective than that of 200 mg·dm<sup>-3</sup> for all the storms monitored. The dry application also was quite effective, although it required at least 10 times more PAM per unit area for the same level of effectiveness [JENKINS *et al.* 2001].

A study on the efficiency of PAM application towards runoff improvement was carried out. The hydrogel was implemented into the soil with a sprinkler using wastewater and freshwater. PAM at different rates – 0, 2.0 and 6.0 kg·ha<sup>-1</sup> was applied on three different soil textures (sandy loam, loam, and silty clay loam) and three irrigations were used, but only the first contained PAM. The research of soil erosion and infiltration was conducted in the laboratory, using a rainfall simulator. It was shown that in the case of loam soil, a smaller dose of PAM (2 kg·ha<sup>-1</sup>) limited runoff by 28 and 25% with the application of freshwater and wastewater, respectively, but was not effective in the case of the second irrigation when using wastewater. For silty clay loam, the dose at 6.0 kg·ha<sup>-1</sup> PAM was required to reduce runoff and soil erosion in the first and second irrigation using freshwater. While using wastewater, 2.0 kg·ha<sup>-1</sup> PAM reduced the runoff and soil erosion by 32 and 46%, respectively, in the first irrigation event, however, the reduction did not occur in subsequent irrigation events. The fact is explained by the possibility of the loss of PAM via the bonding of PAM with solids present in wastewater [SEPASKHAH, BAZRAFESHAN-JAHROMI 2006].

Examples of hydrogel additives applications improving the soil structure or limiting erosive processes are shown below (Tab. 1).

**Table 1.** Examples of synthetic polymers applications towards improving the soil structure or limiting erosive processes

Polymer	Country	Soil kind	Dosing mean	Benefits for soil	Literature
Anionic polyacrylamide	Western Murray Valley of NSW, Australia	hardsetting soils, structurally unstable soils	dry application 5 kg·ha <sup>-1</sup>	PAM – decrease of turbidity to the same level as the lowest rate of gypsum (25 kg·ha <sup>-1</sup> )	DEERY <i>et al.</i> [2002]
Anionic polyacrylamide	California	sandy soils	wet application 3–7 kg·ha <sup>-1</sup>	PAM eliminated sediment in runoff from furrow irrigation; 15–50% infiltration increase	SOJKA <i>et al.</i> [2007]
Polyacrylamide	Isfahan province, central Iran	sandy loam, loamy, clay.	dry application 8 g·kg <sup>-1</sup>	increase of available water content by 1.8-fold of control in clay and 2.2 to 3.2-fold in loamy and sandy loam soil	ABEDI-KOUPAI <i>et al.</i> [2008]
Polyacrylate	Kampala, Uganda	sand, loam, silt loam, sandy loam and clay soils	dry application 0.2 and 0.4% in dry soil	increase of plant available water (PAW) (3-fold in sand, 2-fold in silt loam and 1-fold in sandy loam, loam and clay soils)	AGABA <i>et al.</i> [2010]
Potassium polyacrylate	Bogucin on the Nałęczów Plateau (Lublin Upland)	loess soil	dry application 1 g·kg <sup>-1</sup> or 2 g·kg <sup>-1</sup> in dry soil	decrease of aggregates content above 10 mm; increase of aggregates with dimension of 0.25–10 mm; increase of water-resistant aggregates	PALUSZEK [2010]
Polyacrylamide co-polymer and polyacrylate	Kimberly, USA	degraded calcareous silt loam	one-time addition of hydrogels at 0.25 or 0.5% in dry weight	improvement of water retention and plant available water	LENTZ [2020]

Source: own elaboration based on literature.

Numerous studies indicated that especially PAM has a positive impact on the improvement of soil structure. Research shows that PA applied towards erosion control, reduced the content of sediments in the runoff by an average of 94%, and increased infiltration compared to control by 15–50% on medium to fine-textured soils. Unfortunately, PAM can contain infinitesimal quantities of acrylamide monomer (<0.05%), which may lead to doubts about its security of use [SOJKA *et al.* 2007]. Hence, many studies are carried out in the area of the preparation and application of natural polymers. Polysaccharides belong to a class of biopolymers commonly used in soil-conditioning processes [BEN-HUR, LETEY 1989; SOJKA *et al.* 2007]. Farmers, environmentalists, engineers of the polymer industry, are interested in the development of studies on biopolymer substitutes of PAM, because biopolymers are considered less toxic and fully biodegradable.

### EROSION PROCESSES LIMITATION WITH THE USE OF BIOPOLYMERS

In the last decade, much research on the preparation and application of hydrogels obtained based on natural polymers was carried out [ENGELBRECHT *et al.* 2014; GUILHERME *et al.* 2015; LIU *et al.* 2011; ZHANG *et al.* 2007]. Natural polymers or natural modified, which are alternatives to PAM, were tested in different applications [ISMAIL *et al.* 2013; LU *et al.* 2009]. Hydrogels obtained on the basis of non-toxic biopolymers (lignin, starch, sugar, cellulose, chitosan, gelatine) are considered fully biodegradable [GUILHERME *et al.* 2015; 2017; TOMADONI *et al.* 2019]. Natural hydrogels used as a soil amendment have a positive effect on the improvement of its structure and water retention [GUILHERME *et al.* 2015; LEE *et al.* 2013; LÓPEZ-VELÁZQUEZ *et al.* 2019]. Some studies on the efficacy of biopolymers indicate the effects obtained using natural hydrogels are comparable, and sometimes even better, relative to the use of synthetic polymers [WOODHOUSE, JOHNSON 1991]. Biopolymers are often by-products of various technological processes therefore they are relatively cheap and easily available material for the production of natural hydrogels [LIU *et al.* 2018; SOJKA *et al.* 2007; TOMADONI *et al.* 2019].

An example of the use of natural, unmodified biopolymers is the extraction of mucilage from seeds of *Capsella bursa-pastoris* (L.) Medik. The study carried out by ENGELBRECHT *et al.* [2014], confirmed that mucilage improves seed adhesion to soil particles, reducing seed loss through erosion. The addition of mucilage stabilises the soil structure, increases water retention, and reduces hydraulic conductivity of soil by reducing the porosity from  $0.62 \text{ m}^3 \cdot \text{m}^{-3}$  to  $0.59 \text{ m}^3 \cdot \text{m}^{-3}$  [DENG *et al.* 2012; ENGELBRECHT *et al.* 2014; PENG *et al.* 2011]. The analysis of the results showed also that the mucilage preparation from *Capsella bursa-pastoris* (L.) Medik has a beneficial effect on the soil structure by improving the aggregation of its particles. Good retention properties of the preparation were revealed after the soil was dry [GUILHERME *et al.* 2015].

An experiment using rice straw (RS)-based hydrogels was carried out in El-Saff-Giza Governorate, Egypt. Hydrogels tested in the experiment were prepared under grafting conditions, using acrylonitrile or partially cyanoethylated RS. Biopolymer was used as soil conditioner for sandy calcareous soil. The hydrogels were used at two rates: 2 and  $4 \text{ g} \cdot \text{kg}^{-1}$  soil. The soil properties were determined after the third growing season. The effects observed

were as follows: 1) increase of moisture in the soil and ion mobility; 2) increase of availability of some nutrients; 3) decrease of soil macro-porosity; 4) improved biological activity of the soil; 5) 20% limitation of irrigation water usage [EL-SAIED *et al.* 2016].

In the experiment carried out by WEI *et al.* (2016) polyaspartic acid (PASP) was applied. The biopolymer is a macromolecular amino acid derivative of aspartic acid as monomer, which naturally occurs in many kinds of molluscs. The biopolymer was obtained by crosslinking the hydrophobic PASP backbones. It is biodegradable and possesses biological compatibility. In the experiment, the PASP was used as the water retaining sorbent, on planting *Xanthoceras sorbifolia*, in the mountains of the Mount Daqing National Nature Reserve that has a semi-arid continental climate. The plants in the area are subjected to drought stress. The addition of the PASP hydrogel improved the survival rate of seedlings. It was shown that hydrogel can be useful in ecological restoration as well as in soil and water conservation [WEI *et al.* 2016].

The effectiveness of the use of solutions of natural polymers was tested for the purpose of limitation of irrigation-induced erosion in lab-scale furrow experiments. The solutions of natural polymers (cellulose xanthate, starch xanthate, chitosan, acid-hydrolysed cellulose microfibrils) were prepared at concentrations of 80–120 ppb and were compared with PAM solution at 5–10 ppb. The solutions of biopolymers were less effective than the PAM solution. Natural polymers reduced soil run-off by about 79–80%. The addition of PAM at a concentration at 5 ppb reduced soil run-off by 97%. Only chitosan added at a concentration of 20 ppb, in laboratory conditions, was as effective as PAM at concentration of 10 ppb. Unfortunately, in field tests, chitosan did not reduce irrigation-induced soil losses effectively [ORTS *et al.* 2001].

Cellulose obtained from the processing of conifers was used to improve the stability of clay soils and to reduce the leaching of sediments during heavy rainfall. The use of cellulose preparations together with PAM had a positive effect on the soil structure. A comparable, beneficial effect of reducing sludge eluting appeared after adding several times larger amounts of cellulose than PAM. When PAM was used, the sludge outflow was reduced by 60–80%. After using cellulose microfiber in an amount 8–10 times greater than PAM, the outflow was 88% lower [ORTS *et al.* 2007].

Hydrogel preparations based on modified starch are used in many agricultural applications. Starch is a natural polysaccharide stored in the chloroplast of green leaves and the amyloplast of seeds, pulses, and tubers. Starches can be modified by chemical methods, introducing ionic or hydrophobic groups, which change the viscosity of the starch solution. In the case of preparation of starch-based hydrogels, cross-linking processes are necessary [ISMAIL *et al.* 2013].

Starches etherified with substituted hydroxyl groups by ether groups and grafted starches, are used in the preparation of hydrogels. Starches modified using various vinyl monomers, such as acrylamide and acrylic acid, are used in order to form crosslinked adsorbents with high swelling capacity in water. Despite the chemical modification, starch-based hydrogels are considered fully biodegradable [ISMAIL *et al.* 2013]. Starch-based biodegradable polymers can be used as mulch film and fertilisers for controlled release of materials [LU *et al.* 2009]. Studies show that the use of starch-based preparations improves the use of



nutrients, and the water-holding capacity of the soil (e.g., water-holding capacity without starch-based hydrogel was 30.56%, with the prepared hydrogel was 42.53%) [ISMAIL *et al.* 2013].

Other studies compared the properties of natural derivatives of polysaccharides obtained from bean seeds [YUAN-YUAN *et al.* 2018]. On a slope with loess soils, the use of two derivatives of natural polymers was tested: a neutral polysaccharide and a cationic polypropylene. The use of polysaccharide derivatives resulted in an improvement in soil structure and infiltration (IR) of rainwater [LIU *et al.* 2018; YUAN-YUAN *et al.* 2018].

The application of a neutral polysaccharide in the amount of 1 g improved the rainfall infiltration rate by 22.81%, and in the amount of 3 g by 13.69%. After the addition of the cationic form of the polymer (modified polysaccharide), in the amounts of 1, 3, and 5 g, the infiltration increased by 39.47%, 46.59%, and 46.50%, respectively. Thus, higher infiltration values were obtained for the cationic polysaccharide. Higher doses of the inert polymer (5 g·m<sup>-2</sup>) deteriorated infiltration due to the high viscosity of the solution. Analysing the size and stability of soil aggregates, it was found that after using a cationic polymer, the number of aggregates with size >0.25 mm increased from 27.19 to 90.42% before rainfall and from 9 to 50% after rainfall [YUAN-YUAN *et al.* 2018]. It was found that the cationic form of the polysaccharide is more soluble and forms less viscous solutions than polyacrylamide hydrogel preparations with similar concentrations (PAM) [SANTOS *et al.* 2003; YUAN-YUAN *et al.* 2018]. Additionally, some authors indicated that hydrogels obtained on the basis of polysaccharides are better soluble in water and possess lower viscosity compared to PMA [AGASSI, BEN-HUR 1992].

In the case of polysaccharide amendments which are extracted from bean embryos, no disturbing test results were reported. It has been shown that applied polysaccharides have no irritating or adverse effects on aquatic species [YUAN-YUAN *et al.* 2018].

LEE *et al.* [2013] tested a hydrogel prepared on the basis of biopolymers, lignin and corn flour, which displayed comparable effects to the commercial use of anionic polyacrylamide (PAM) [LEE *et al.* 2013; LEE, YANG 2004]. The modified natural hydrogel was obtained from a mixture of lignin and cornmeal with acrylamide (AMD) and acrylic acid (AA) monomers. The experiments were done on a field with a 36% slope and with a 20 mm·h<sup>-1</sup> simulated rainfall. After the application of each hydrogel (PAM and PB), at a rate of 200 kg·ha<sup>-1</sup> to loamy sand soil, in both cases, the water holding capacity increased by an average of 32.6% compared to the soil without the addition of polymers. The use of both hydrogels made it possible to obtain more stable soil aggregates facilitating infiltration. The stability of soil aggregates improved for soils treated with PAM and BP, by 25.4 and 27.1%, respectively, compared to untreated soil [LEE *et al.* 2013].

A polymer obtained on the base of guar gum can be a promising soil conditioner agent useful in agriculture applications. It was confirmed that the hydrogels synthesised by grafting guar gum with acrylic acid and cross-linking with ethylene glycol dimethacrylic acid could absorb up to 800 cm<sup>3</sup> of water per gram. This modified natural hydrogel, introduced into the soil, improved its porosity, moisture absorption, and retention capacity significantly. Its application was tested in a soil containing 60.5% of sand, 18% of silt, and 21.5% of clay. This hydrophilic hydrogel was introduced into the soil at a minor dose of 0.1–0.3%.

Fine powder of hydrogel introduced to the soil at a dose of 0.3% improved its porosity up to 9% of its original. The water holding capacity of the soil was increased up to 1.5 times. Studies confirmed that obtained polymer is biodegradable and possesses a half-life period of 77 days of biodegradation in soil. In the first 56 days, about 40% of the hydrogel was decomposed in the soil, while only 11% weight loss was observed from 56 to 100 days. 30% weight loss was noted from 100 to 180 days [THOMBARE *et al.* 2018].

Cellulose microfibrils, acid-hydrolysed, were tested for their ability to decrease sediment leaching from furrows in experimental plots with a 10% slope. Their efficiency compared with PAM was less. Tests indicated that microfibrils reduced sediment run-off by 88% in the case of eight- to tenfold higher concentrations than during PAM application. Despite the necessity of the use of a higher concentration of natural polymer, cellulose microfibrils can be a biodegradable alternative to PAM [ORTS *et al.* 2007].

The described examples of biopolymers used for the improvement of soil structure are listed in Table 2. On the basis of mentioned examples, it can be concluded that polymers obtained on the basis of natural biopolymers show a positive influence on soil conditions, similarly to synthetic hydrogels. The addition of natural polymer results in an increase of the number of aggregates with dimensions of 0.2–10 mm, an increase of the soil water-holding capacity, and a reduction of sediments run-off. Unfortunately, natural amendments, compared to synthetic polymers, improve infiltration and surface runoff to a lesser extent, which makes it necessary to apply them in greater quantities. The differences are especially seen compared to PAM. Modification of natural polymers via acrylates raises reservations due to the use of harmful monomers. The polymers that are not crosslinked with acrylates are particularly promising as a potential replacement for synthetic polymers [GUILHERME *et al.* 2015]. Despite this chemical modification, natural polymers are indicated as a biodegradable alternative for synthetic polymers [GUILHERME *et al.* 2015; THOMBARE *et al.* 2018].

## HYDROGEL APPLICATION SECURITY

In agricultural applications, the security of amendments added to soil is very important. SAPSs based on synthetic polymers are characterised by low cost, long service life, and high-water absorption rate. Unfortunately, the safety of their application raises some doubts and is the subject of many studies.

Among popular synthetic polymers, the most commonly used are the following: linear polyacrylamide for sprinkler irrigation, crosslinked polyacrylic acid, polymethacrylic acid, or polyacrylamide which are applied in solid form. There are rationales that synthetic polymers PAA and PAM may contain carcinogenic and neurotoxic AA and AMD monomers in their structure. Therefore, polymer products are carefully checked in respect to the level of contamination with harmful monomers. Permissible maximum trace amounts of monomers, well below the permissible limits. For this reason, in the case of PAA, residual AA present in the polymer are neutralised by combining the polymer with sodium or potassium hydroxide during their production [DELL'AMBROGIO *et al.* 2019; ZOHURIAAN-MEHR, KABIRI 2008].

**Table 2.** Examples of natural polymers applications for improving soil structure or limiting erosive processes

Polymer	Country	Soil kind	Dosing mean	Benefits for soil	Literature
Polyaspartic acid	China, Mount Daqing National Nature Reserve	mountain, semi-arid continental climate	dry application 25 g per hole under seedling	useful in ecological restoration as well as in soil and water conservation	WEI <i>et al.</i> [2016]
Rice straw (RS)-based hydrogels	El-Saff-Giza Governorate, Egypt	sandy calcareous soil	dry application (2 and 4 g·kg <sup>-1</sup> )	increase of moisture in the soil; decreasing soil macro-porosity; 20% limitation of irrigation water usage	EL-SAIED <i>et al.</i> [2016]
Natural polymer derivatives, (neutral polysaccharide)	Loess Plateau, located in northern Shaanxi Province, China	silt loam soil contents of organic matter, clay, silt and sand	wet application (0–5 g·m <sup>-2</sup> )	increase of rainfall infiltration; increase water-stable soil aggregates >0.25 mm	LIU <i>et al.</i> [2018], YUAN-YUAN <i>et al.</i> [2018]
Hydrogel – grafting guar gum with acrylic acid and cross-linking with ethylene glycol dimethacrylic acid	Southern Portugal	soil containing of sand, silt, clay	dry application (0.1, 0.2 and 0.3% w/w)	improvement of porosity up to 9% of its original level; the water holding capacity of the soil was increased up to 1.5 times	THOMBARE <i>et al.</i> [2018]

Source: own elaboration based on literature.

An example of such a neutralised polymer may be the commercially available sodium or potassium polyacrylate. The results of safety studies on these polymeric salts showed the presence of only trace amounts of acrylic acid monomers. It should be remembered that during decomposition, potassium ions will pass into the soil, their presence in soil is beneficial for plant development. The situation is different in the case of sodium preparations, where excess sodium may have a negative effect on yield. Sodium polyacrylates are not recommended in agriculture applications [KULIKOWSKI *et al.* 2018].

The toxicity of hydrogels on the basis of PAM was tested towards widespread species of shellfishes, fishes and algae, which are commonly used for freshwater toxicity testing, such as *Hyalella azteca*, *Chironomus dilutus*, *Pimephales promelas*, *Selenastrum capricornutum*. Five PAM formulations, prepared in the way of oil-based products (two products), water-based product, granular product, and tablet product, were evaluated for toxicity. In the case of oil-based products, often used for erosion control, acute toxicity was seen at concentrations less than 10 mg·dm<sup>-3</sup>. Other products indicated minimal toxicity even in the case of concentrations 10 times those used in agriculture. Obtained results indicated that, in the case of oil-based products, the reason for their toxicity was rather surfactants or emulsifiers, not PAM itself [WESTON *et al.* 2009].

Research shows that the degradation of polymers on basis of PAM and PAA in the soil is a multi-stage process [STAHL *et al.* 2000]. Unpolymerized monomers or low molecular weight oligomers, which in fact are impurities of the actual polymer, are easiest to break down and mineralise [COOK *et al.* 1997]. The next process is the degradation of the three-dimensional structure of the hydrogel, which leads to the release of linear polymers, which next are dissolved in the soil solution [LENTZ 2020].

In the first step of degradation, both PAM and crosslinked PAA are broken into smaller fragments via abiotic mechanisms. Only then is it possible for these smaller particles to be absorbed and broken down by microorganisms [DELL'AMBROGIO *et al.* 2019; HAYASHI *et al.* 1994]. The final degradation products of PAM are expected to be carbon dioxide and ammonia or nitrogen [CAULFIELD *et al.* 2002; DELL'AMBROGIO *et al.* 2019; SMITH, OEHME 1991]. Therefore, research on the potential harmfulness of the use

of synthetic polymers should demonstrate what products may appear during hydrogel decomposition and whether they might pose a threat to the natural environment [DELL'AMBROGIO *et al.* 2019; XIONG *et al.* 2018].

The degradation rate of PAMs and PAAs in the environment is dependent on temperature, sunlight, pH, humidity and salt content [BARVENIK 1994; DELL'AMBROGIO *et al.* 2019; LIANG *et al.* 2018; SOJKA *et al.* 2007]. It was confirmed that chemical, photolytic and thermal decomposition of PAM can lead to the formation of ketones, aldehydes, and carboxylic groups [XIONG *et al.* 2018]. Numerous studies have shown that undesirable amounts of AMD (acrylamide), AA (acrylic acid), PAA may be produced during the degradation of linear PAM or crosslinked polymers of PAA or PAM [BOLOGNA *et al.* 1999; CAULFIELD *et al.* 2002; DELL'AMBROGIO *et al.* 2019]. These new molecules, with a lower atomic mass, are usually more hydrophilic, which means that they can more easily enter the groundwater and thus pose the risk of contamination [DELL'AMBROGIO *et al.* 2019].

It has been shown that the degradation of linear PAM leads to the release of AA monomers [DELL'AMBROGIO *et al.* 2019], and under anaerobic conditions, some amounts of intermediate products, like AMD, AA and PAA can be emitted [WANG *et al.* 2018]. Dimer and trimer fragments may be formed during the degradation of polyacrylic polymers [DELL'AMBROGIO *et al.* 2019; MCNEILL, SADEGHI 1990]. When degradation of linear or crosslinked PAM was carried under conditions of higher temperature, at 95°C, or under irradiation with UV, small amounts of AMD (<50 ppm) were detected. A positive conclusion was the fact that emerging monomers and dimers are not toxic to microorganisms which are responsible for their relatively quick mineralisation [DELL'AMBROGIO *et al.* 2019; LARSON *et al.* 1997; SUTHERLAND *et al.* 1997].

Research on linear and crosslinked PAM degradation confirmed that at room temperature, under typical environmental conditions, the degradation of linear PAM should not lead to AMD release, while the degradation of crosslinked PAM might lead to AMD release under high temperatures [CAULFIELD *et al.* 2002; 2003; DELL'AMBROGIO *et al.* 2019]. Although the levels of released AMD were below legal limits for commercially manufactured PAM products in Europe, it was concluded that,

because of the possibility of formation of higher amounts of AMD at 35°C, PAMs may be unsuitable for warm climates.

A lot of research was carried out in order to estimate the average degradation rate of synthetic polymers. Literature data concerning the degradation time of polymers in the soil are not unambiguous. Some studies show the decomposition of polyacrylic polymers may take several days [COOK *et al.* 1997; STAHL *et al.* 2000], but other researchers estimate the decomposition time to be several months or years [HOLLIMAN *et al.* 2005; OKSIŃSKA *et al.* 2016; STAHL *et al.* 2000]. In the majority of cases, the percentage degradation of PAA SAPS did not exceed a few percent per year. The degradation rate of acrylate-based hydrogels in compost was 5.9% under aerobic conditions after about 500 days [STEGMANN *et al.* 1993]. For PAA SAPS, a study showed a mineralisation rate of 0.12–0.24% during six months in agricultural soil, under common environmental conditions [WILSKE *et al.* 2014]. In the case of waterborne PAA forming fertiliser coating in agricultural field soil, polymer degradation led to a weight loss of 1.77 % after 12 months [LIANG *et al.* 2018]. HÜTTERMANN *et al.* [2009] reported biodegradation of PAA and PAM at a similar range, from 1 to 9% per year, similarly to the one of PAMs [DELL'AMBROGIO *et al.* 2019].

Most of the studies confirmed that PAA and PAM polymers, especially crosslinked, indicate a low degradability in soil and are relatively resistant to microbial attack. Therefore, it is estimated that the decomposition of crosslinked polymers is not more than 10% per year. The rate of hydrogels' decomposition depends on their structure and composition. Linear PAMs seem to degrade faster than crosslinked PAMs, while crosslinked PAAs seem to be even more resistant. The researchers' results showed that polymers indicated a decomposition rate comparable to the decomposition of natural organic matter in forest ecosystems.

In spite of extensive research, the risk of releasing hazardous monomers has still not been ruled out from the degradation of synthetic SAPs [CAULFIELD *et al.* 2002]. In the case of both polymers, PAM and PAA, data about their degradation were received mainly based on controlled laboratory conditions. Such artificial conditions might not reflect adequately the field conditions. For these reasons, long-term studies on the behaviour of PAMs and PAAs in the soil are still needed [DELL'AMBROGIO *et al.* 2019; XIONG *et al.* 2018]. Interesting results were provided by a 9-year-long experiment carried out with crosslinked polymers based on polyacrylic and polyacrylamide. Their long-term behaviour in soil was studied. In the course of hydrogel degradation, cross-linkages are destroyed first, resulting in the breakdown of the gel structure. The crosslinked structure is responsible for its water absorbing and retention capacity. Therefore, a measurable indicator of hydrogel activity is its ability of water adsorption and desorption. The measurements of soil water retention and plant available water (PAW, g water·g<sup>-1</sup> dry soil) were carried out in soil samples for seven out of the nine years of the experiment.

The best results of the increase of plant available water (PAW, g water·g<sup>-1</sup> dry soil) were obtained in the case of crosslinked polyacrylamide. The best result obtained in the first year after hydrogel application decreased linearly in the following years. It has been calculated that favourable water retention resulting from the presence of the polymeric additive may be significant for 24–29 years from the first hydrogel application, while hydrogel's producers declare five years of hydrogel

effectiveness [LENTZ 2020]. The investigations showed that polyacrylamide might possess long-standing abilities for increasing soil water retention. These results indicate that caution should be exercised with the use of this type hydrogel, especially in areas where there may be rainfall that exceeds the needs of the crops [EL-HADY *et al.* 1990; ISLAM *et al.* 2011; LENTZ 2020]. Additionally, increased water retention could slow soil drying and warming in the spring, and delay tillage and planting [LENTZ 2020].

It is well known that polymers based on natural polymers, such as cellulose, starch and chitosan, are easier biodegradable. Nevertheless, their lower ability of water absorption and lower efficacy of activity causes the necessity to use larger doses [WEI *et al.* 2016]. In order to enhance the efficiency of natural SAPSs and to improve their stability, it is necessary to cross-link natural polymers. In this way, biopolymers on the basis of Arabic gum or other polysaccharides are formed through reaction with acrylamide and acrylate monomers [GUILHERME *et al.* 2015].

It is postulated that SAPSs obtained on the basis of natural polymers are easier to decompose and are less burdensome for the environment, but also biopolymers obtained using natural polymers like polysaccharides are recommended as completely safe soil additives. In the light of the presented studies on synthetic polymers security, it can be concluded that synthetic hydrogels, tested and used in accordance with the manufacturer's recommendations, do not pose a threat to the environment [GUILHERME *et al.* 2015; LU *et al.* 2009; ORTS *et al.* 2001]. It should be mentioned, however, that hydrogels are relatively new preparations recommended for use in agriculture. Both in the case of synthetic hydrogels and biopolymers, the results of long-term studies are lacking, which have been conducted over a period of more than two years. Such studies are needed to help to verify data on the actual long-term retention of hydrogels in the soil.

## YIELD IMPROVEMENT

Adverse physical and chemical soil properties, such as low infiltration rates as well as low water retention, are factors which often cause a decrease of crop productivity. The water and nutrient holding capacity of sandy and permeable soils, in particular, are extremely limited. These soil types are characterised by excessive drainage of rain and irrigation water, as well as nutrients leaching below the root zone [AJWA, TROUT 2006; EL-HADY *et al.* 1990; KAZANSKII, DUBROVSKII 1992].

In arid regions of the world, the use of super absorbent polymers (SAPs) may effectively increase water and fertiliser use efficiency in crops. When polymers are incorporated with soil, it is presumed that they retain large quantities of water and nutrients, which are released as required by the plant. Thus, plant growth could be improved with a limited water supply [ISLAM *et al.* 2011].

The addition of synthetic hydrogels can increase the water retention capacity of the soil by up to 50–70% depending on the type of hydrogel and the proportion of its mass to soil mass [NEETHU *et al.* 2018]. In the 1980s it was confirmed that the addition of a hydrogel significantly increases the water capacity of sand from 171 to 402%, thereby reducing the water stress of plants. The application of hydrogels shifts the permanent wilting point (PWP). PWP was reached after 6–7 days for sand enriched with polymer in a dose of 1 g·kg<sup>-1</sup> sand and after 9–10 days for



a polymer at the dose of 2 g·kg<sup>-1</sup> of the sand. In contrast, in the control sample of sand without hydrogel additives, the PWP was achieved after 2–3 days [LENTZ 2020].

The essential issue is the improvement of germination and yield. The dose of 7 kg·ha<sup>-1</sup> of PAM improved cotton germination by 84% [CHAN, SIVAPALAN 1996]. It was found that the addition of PAM in the amount of 0.001, 0.005, and 0.01% in dry soil (clay with clay minerals) improves the germination of cotton seeds by reducing the penetration resistance [SIVAPALAN 2002]. Other studies showed an increase in the yield of pea on sandy soils by approx. 23% with the dose of PAM hydrogel in the amount of 25 g·m<sup>-2</sup> and the necessary irrigation [OWCZARZAK *et al.* 2006].

Hydrogels are used in seed coating and conditioning. The hydrogel shell ensures the right level of moisture. It can also serve as a matrix for minerals or protective measures necessary for the proper growth of the plant. The use of seeds prepared in this way allows reducing the amount of fertilisers used later [KULIKOWSKI *et al.* 2018].

Hydrogels also work well in the encapsulation of the root system of seedlings in order to extend their survival in drought. Potassium polyacrylate (Aquaterra) was used for this purpose in the Niepołomice Forest District (near Krakow, Poland). The survivability of seedlings of *Pinus sylvestris* L. covered and planted after 1–12 days of their storage during drought was on average 30% higher in comparison to the control part [BARTNIK 2008].

The use of potassium polyacrylate was also tested in a forest nursery in Julinek (Poland) on sandy soils. Substrates with the addition of hydrogel in amounts up to 0.04% were characterised by higher moisture content, longer water retention in the soil, slower drying rate (by 2–4 days) compared to the substrates without the addition of hydrogel. After applying the hydrogel to the substrate, the tests showed an increase in capillary capacity and total water capacity. The hydrogel contributes to the improvement of the loosening of the tested horticultural substrates. Higher doses of hydrogel indicated a significant effect on the water retention capacity and stimulated the growth of cucumber seedlings [LECIEJEWSKI 2008].

Experiments were carried out to improve cucumber (*Cucumis sativus* L.) cultivation on sandy soils in El-Katta (Giza). A mixture of acrylic and acrylamide, anionic-cationic hydrogels were used. Gel doses were introduced to a depth of 15 cm. After using hydrogels, the need for irrigation was reduced from 100 to 85%. The yield of cucumber cultivation also increased by 38.6, 54.2, and 78.3% in relation to the crops without the hydrogel, after adding the hydrogel in the amount of 2, 3, and 4 g of hydrogel per seedling, respectively. Limiting irrigation to 70 and 50% of the water demand of plants in all tested cases resulted in a decrease in yields. However, the yield was higher each time after using the hydrogel [EL-HADY, WANAS 2006].

Comparative studies of cationic and anionic hydrogels in a climate typical of arid lands were conducted in northern China [XU *et al.* 2015]. In the Wuchuan County region, the effects of synthetic potassium polyacrylate (PAA), anionic polyacrylamide (PAM), and humic acids of the natural origin (HA) were tested on sandy loam soils in potato cultivation for three years. The additives were used individually or in a mixture of synthetic and natural additives. The doses were 45 kg·ha<sup>-1</sup> for hydrogels and 1500 kg·ha<sup>-1</sup> for humic acid. Both types of hydrogels mixed with humus acid significantly improved water retention. An increase in potato yield from 4.2 to 32.9% was observed, as well as an

increase in the fraction of tubers weighing more than 150 g, and a decrease in the fraction of tubers weighing less than 75 g after the application of soil additives. The best potato yielding results were obtained after applying polyacrylamide (PAM) with humic acids (HA).

The hydrogel obtained from a mixture of natural polymers (lignin, corn meal) and acrylic and acrylamide monomers showed a slightly less pronounced effect on the improvement of the germination rate of Chinese cabbage seeds, compared to the treatment with PAM. However, the increase in leaf length was greater after the application of PB (by 16.7% compared to the control without the addition of polymers and by 4.6% compared to PAM). On the other hand, the degree of N and P leaching from the soil was greater after the application of PAM [LEE *et al.* 2013].

It has been shown that the use of starch copolymers improves the growth of lettuce and barley as well as extends the survival of plants on sand during a drought period [MONTESANO *et al.* 2015]. In another investigation, a starch hydrogel was obtained by grafting copolymerisation using acrylamide, acrylic acid, and polyethylene glycol mas a crosslinker via gamma-ray radiation technique. Studies on the influence of hydrogel on the germination of corn seeds and the growth of young plants showed a satisfactory effect on the weights of leaves and roots of the plants when hydrogel addition was 0.2 % w/w [ISMAIL *et al.* 2013].

In studies carried out by Brazilian researchers, a biodegradable hydrogel based on modified cellulose hydrogel was used in the cultivation of eucalyptus. The benefits of using hydrogel and its biodegradability were investigated. The soil used was sampled at Sorocaba in the State of São Paulo, Brazil. Prepared soil samples consisted of 23% sand, 23% cattle manure, 23% soil and 31% water. The applied hydrogel reduced fertiliser leaching and improved the efficiency of eucalyptus seedlings and reduced their mortality. Additionally, the cellulose preparation was non-toxic, biodegradable, and therefore environmentally friendly [SENNA, BOTARO 2017]. Also, pectin-based hydrogels used as carriers of nutrients show the ability to control the release of urea, phosphate, and potassium [GUILHERME *et al.* 2015].

The presented examples show the benefits of using both synthetic and natural soil SAPSs. Hydrogels are used not only to reduce the frequency of irrigation but also to improve the soil structure and reduce its susceptibility to erosion. An important application of hydrogels, especially based on natural polymers, is the possibility of controlled release of nutrients, thus reducing fertiliser losses and protecting the environment.

## CONCLUSIONS

Water resources are an indispensable element of the correct functioning of natural systems, including agriculture. Water availability largely determines the yield of farming. Therefore, various methods are employed to improve water retention.

SAPS, due to their ability to absorb large amounts of water and to release it gradually, are excellent soil additives providing water retention. Since the 1990s, the use of polymer soil additives has been considered by many researchers and government institutions as one of the best possible agricultural practices (BMPs). The cost of hydrogels application should be recompensed to agricultural producers by higher yields.



The use of SAPSs reduces water stress in field crops and influences the optimisation of water availability, especially in dry regions. It is estimated that even 0.2% addition of a hydrogel provides a 10–35% increase in water content in sandy soils. The addition of SAPSs in the dose of 50–140 kg·ha<sup>-1</sup> on sandy soils increases the productivity to the level that is achievable after adding hundreds of tons per hectare of alluvial sediments.

Hydrogels are used in order to improve soil properties such as increased infiltration rate and reduction of surface runoff. The increase of soil infiltration is beneficial, especially in clay or salt-rich soils, in order to improve the efficiency of irrigation. Polymeric addition limits surface runoff, hence also limiting the erosion caused by soil leaching. Soil application of PAM leads to the stabilisation of soil aggregates, to soil aeration improvement, and increases water permeability or retention.

The most popular hydrogels used in agriculture are hydrogels based on synthetic polymers, due to their commercial availability and low cost. Among synthetic polymers, the most commonly used agricultural applications are linear or crosslinked polyacrylic acid, polymethacrylic acid, and their salts and polymers on the basis of crosslinked polyacrylamide. SAPSs possess undoubted advantages. They are produced on the basis of relatively cheap synthetics, such as polyacrylic acid and polyacrylamide, display long service life and ability of absorption of a large quantity of water, however their degradation is long-term and therefore may exert adverse effects on the environment and on plant growth. Therefore, apart from synthetic polymers, also modified natural polymers are used. Biopolymer SAPSs obtained based on natural polymers, such as cellulose, starch, and chitosan, possess an obvious advantage of degradability. Nevertheless, PAM efficacy is five to six times more at a much lower concentration in comparison to biopolymers.

Biopolymers indicate a lower ability of water absorption than synthetic polymers, and thus have to be used in a larger amount. Biopolymers are also less effective in improving the rate of infiltration or reducing leachate compared to synthetic polymers. Biopolymers are prone to rapid degradation, so in order to ensure their stability in soil and to improve their adsorption properties they must be modified in cross-linking processes. One way is chemical cross-linking by introducing acrylate monomers. The modified natural polymer can be a potential source of harmful monomers during the decomposition of the hydrogel. Despite these modifications, it is postulated that the polymers obtained on the basis of natural polymers are easier to decompose and are less burdensome for the environment.

The literature overview indicated the anionic PAM, cross-linked or non-crosslinked, was used in many applications and showed good efficiency in the improvement of yield and soil condition. Unfortunately, the literature reports concerning the possibility of occurrence of residual of acrylamide monomers in PAM might raise some doubts concerning the safety of its application. Polyacrylamide is non-toxic to humans, animals, fish and plants, but residual monomer (acrylamide) which can be present in polyacrylamide hydrogels is a neurotoxin dangerous to humans. Therefore, the safe use of synthetic polymers requires a strict regime to control the residual monomer in the polymer product intended for agricultural purposes. If the content is negligible, PAM itself poses no environmental risk.

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