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Chapter 4

Hydrogels from Fundaments to Application

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Abstract

Polymer superabsorbents commonly known as hydrogels are cross-linked highly molecular compounds able to absorb water from physicochemical fluids in the amounts from 10-fold to 100-fold larger than their dry mass. Numerous investigations have shown that they can help reduce irrigation water consumption, lower the death rate of plants, improve fertilizer retention in soil and increase plant growth rate. Besides water absorption and retention, the superabsorbent polymers have many advantages over conventional ones, such as a sustained supply of nutrition to plants for a longer time, thus increasing the phosphate fertilizer use efficiency and decreasing application frequency. The aim of this study is to investigate the influence of chemical conditions on hydrogels, kinetic and absorption behaviour towards metal ions in the presence of the chelating agent of a new generation. In this group, there are IDS, EDDS, GLDA, MGDA, etc. In the chapter, the research on the applicability of the effective absorption of metal complexes with a biodegradable complexing agent will be presented. The possibility of the preparation of slow-release fertilizers of controlled activity of a new generation in such system will also be discussed.

Keywords: superabsorbents, new complexing agents, IDS, EDDS, GLDA, MGDA, absorption, fertilizers

1. Introduction

Superabsorbents were first developed in the early 1960s in the United States Department of Agriculture by grafting acrylonitrile (AN) onto corn starch and saponifying the product. Over the past decades, significant progress has been made in the field of hydrogels as functional biomaterials. Since then in the group of the main global participants on the superabsorbent

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market, Dow Chemical, Hercules, General Mills Chemical, DuPont, National Starch & Chemical, Enka (Akzo), Sanyo Chemical, Sumitomo Chemical, Kao, Nihon Starch and Japan Exlan should be mentioned.

Polymer superabsorbents commonly known as hydrogels are three-dimensional (3D) cross-linked highly molecular compounds able to absorb liquids in the amounts from 10-fold to 100-fold larger than their dry mass. They are hydrophilic, cross-linked, and swelling in water polymer materials. They are sometimes called smart hydrogels as they can absorb up to 1000 g water. The literature reports a number of classifications of hydrogels. As for physicochemical properties, hydrogels can be divided into different modes. There are two main groups of superabsorbents. The first group is physical hydrogels called reversible and they have the 3D network in which the polymer chains are linked by electrostatic forces, hydrogen bonds and hydrophobic interactions. These gels are unstable and upon heating can be converted into a polymer mixture, e.g., gelatin and agar. The second group includes chemically stable gels with the 3D network, in which the polymer chains are linked by stable covalent bonds. Both starch and vinyl monomers such as acrylic acid, acrylamide, acrylonitrile and polyvinyl alcohol are of interest as they contain a number of hydrophilic functionalities in their structures such as hydroxyl and carboxyl groups. The ionic phase of hydrogels usually consists of both groups bound onto the polymer chains (which can be ionized) and a number of mobile ions—counter-ions and co-ions (due to the presence of solvent surrounding the hydrogel). As for the source they can be natural, synthetic and hybrid, as for the cross-linking they are physically and chemically linked and as for degradability they can be biodegradable and non-biodegradable. Homopolymeric, copolymeric and interpenetrating networks (IPN) can be recognized given the way of preparation [1, 2]. Homopolymeric gels contain the same monomers, which are basic structural units. Copolymeric gels comprise two or more different monomer species with at least one hydrophilic component whereas interpenetrating polymers or double networks are formed by swelling of the first network in a solvent containing monomers, which then forms the second intermeshing network structure. The double networks will either be hydrophobic or hydrophilic or the combination of both [3–5]. Depending on the charges of the bound groups, hydrogels can be ionic (cationic or anionic), neutral, amphoteric (ampholytic) containing both acidic and basic groups as well as zwitterionic (polybetaines) containing both anionic and cationic groups in each structural repeating unit. Response hydrogels are biochemically (antigens, enzymes, ligands), chemically (pH, solvent composition, ionic strength, molecular species) or physically (temperature, electric or magnetic field, light, pressure, sound) responsive.

The types of cross-linking agents can also be the criterion of classification. It is also possible to divide hydrogels into groups by their structure that is amorphous, semi-crystalline, crystalline and hydrocolloid aggregates [6].

The phenomenon of liquid absorption is a result of separation of polymer chain network that is manifested by swelling of polymer material assuming the gel form [1]. Hydrogels with characteristic properties such as desired functionality, reversibility, sterility and biocompatibility meet both material and biological requirements to treat or replace tissues and organs or the function of living tissues as well as to interact with the biological system. During years, the

number of hydrogel formulations steadily grew and the problems such as low solubility, high crystallinity, non-biodegradability, unfavourable mechanical and thermal properties were solved. This was due to the combination of natural and synthetic polymers characterized by better biodegradation, solubility, crystallinity and biological activities. To avoid the disintegration (the hydrophilic linear polymer chain of hydrogel can dissolve in water due to the polymer and water thermodynamic compatibility) different cross-linked agents were proposed. Cross-linking can take place *in vitro*, during the preparation, or in vivo (*in situ*) after the application. The hydrophilicity of hydrogel network is due to the presence of hydrophilic groups such as $-NH_2$, $-COOH$, $-OH$, $-CONH_2$, $-CONH-$ and $-SO_3H$, capillary effect and osmotic pressure. It can be chemical or physical in nature. In the case of the chemical cross-linking, the polymer chains are covalently bonded by the cross-linking agent whereas in the case of the physical cross-linking hydrogen bonding, hydrophobic interaction, ionic complexation, post-process bulk modification, reshaping, biodegradation take place [7].

It should be remembered that swelling of hydrogels is a complex process comprising a number of steps. In the first step, the polar hydrophilic groups of the hydrogel matrix are hydrated by water, which appears in the form of primary bound water. In the second step, the water also interacts with the exposed hydrophobic groups and the secondary bound water layer is formed. Both the primary and secondary bound water forms the total bound water. In the third step, the osmotic driving force of the network towards infinite dilution is resisted by the physical or chemical cross-links, so the additional water is absorbed. The water absorbed into the equilibrium swelling is called bulk water or free water, which fills the spaces between the network or chains and the centre of larger pores. The amount of water absorbed by a hydrogel depends on the temperature and specific interactions between the water molecules and the polymer chains. **Table 1** summarizes the classification details for hydrogels.

Physical properties	**Conventional**		**Smart**
Source	Natural	Synthetic	Hybrid
Cross-linking	Physically linked		Chemically linked
Degradability	Biodegradable		Non-biodegradable
Preparation	Copolymeric	Homopolymeric	Interpenetrating network
Ionic charge	Cationic	Anionic	Non-ionic
Response	Physical agents: temperature, pressure, light, electric field, magnetic field		Chemically responsive: biochemical agents, antigens, enzymes, ligands

Table 1. Criterion of hydrogels classification.

2. Hydrogels preparation

Hydrogels can be produced in the form of films, membranes, rods, spheres and emulsions. They can be classed into three categories: starch-polyacrylonitrile graft polymers (starch co-

polymers), vinyl alcohol-acrylic acid co-polymers (polyvinyl alcohols) and acrylamide sodium acrylate co-polymers (cross-linked polyacrylamides) [8, 9]. They can be physical or chemical. Physical gels are obtained due to physical nature of the cross-linking process. This is achieved by physical processes such as hydrophobic association, chain aggregation, crystallization, polymer chain complexion and hydrogen bonding. On the other hand, a chemical process, i.e., chemical covalent cross-linking (simultaneously or post-polymerization) is utilized to prepare a chemical hydrogel. Physical hydrogels are reversible due to the conformational changes where chemical hydrogels are permanent and irreversible because of configurational changes. Another category is the double network hydrogels (interpenetrating networks), formed by the combination of physical and chemical cross-linked hydrogels due to an electrostatic interaction. Recently, they have been employed to overcome the disadvantages of solely using physical or chemical hydrogels with a high liquid uptake capacity over a wide range of pH and a higher sensitivity towards changes in the pH value as compared to chemical hydrogels.

The hydrogels are divided into two main classes, i.e., natural, containing two basic groups based on polypeptides (proteins) and polysaccharides, and another is artificial one [10, 11]. Natural hydrogels are usually prepared by the addition of some synthetic parts onto the natural substrates, e.g., graft copolymerization of vinyl monomers on polysaccharides. The synthetic route for the production of most synthetic hydrogel is the free radical multifunctional vinyl monomers. Each monomer contains a carbon double bond where an active centre can propagate to produce polymer chains. Active centres reaction also depends on the solvents, reaction conditions as well as particular monomers and can be initiated by different factors: heat (thermal initiators), light (photoinitiators), enzymes (bioinitiators) or electron beams. Generally, water-soluble natural or synthetic polymers are cross-linked to form hydrogels in a number of ways, such as (i) linking polymer chains by chemical reaction, (ii) using ionizing radiation to generate main-chain free radicals that can recombine as cross-link joints and (iii) interacting physically such as electrostatics, entanglements and crystallite interactions [12, 13]. Any of various polymerization techniques can be used to form hydrogels, including bulk, solution and suspension polymerizations. The three main components of hydrogels are monomers, initiators and cross-linkers which can be diluted in water or any solvent to control the polymerization heat. However, its disadvantage appears in the form of impurities left from the preparation process containing unreacted monomers, initiators, cross-linkers and side products. Hydrogels are commonly prepared from polar monomers of both natural and synthetic origins by graft polymerization, cross-linking polymerization, network formation in aqueous medium and by radiation cross-linking methods. Their short characteristic is presented below.

Solution polymerization (wherein the polymerization medium is a suitable solvent, which dissolves both monomers and initiator) and suspension polymerization (wherein monomer forming droplets, with the initiator in them, are completely insoluble and suspended in a solution) are the most common techniques for the production of a variety of hydrogel networks by reacting hydrophilic monomers with multifunctional cross-linkers and added initiators.

Polymerization reaction is frequently initiated with radiation, ultraviolet or chemical catalysts. Cross-linking of polymers is due to chemical reaction, ionizing radiation or physical interac-

tions such as entanglements, electrostatics or crystallite formation. In the case of suspension polymerization, monomers and initiator are dispersed in the organic phase. The hydrogel properties depend on the viscosity of the monomer solution, agitation speed, rotor design and dispersant type [1, 14]. Recently radiation polymerization and grafting have been also used. In the case of the block polymerization to the liquid monomer, an initiator is added directly and the obtained hydrogels are characterized by inherent weak structure therefore they are frequently grafted. The suspension-gelation method (microcapsule templating method) was also described to prepare macroporous polymeric hydrogels [15]. An aqueous suspension is formed by dispersing the microcapsules as a pore template (porogen) into a pre-gel aqueous solution containing monomers and cross-linking monomers. Then, a composite hydrogel containing distributed microcapsules is prepared by copolymerizing the pre-gel aqueous solution. Finally, a macroporous hydrogel is obtained by breaking down the structure of the microcapsules dispersed in the composite hydrogel with a chemical treatment. The suspension-gelation method is conducted using only low toxic and inexpensive physically cross-linked microcapsules such as calcium alginate gel. Graft copolymerization resulting in development of physical and chemical properties of hydrogels makes them excellent smart materials [16–18].

Hydrogels originating from microbial poly(γ-glutamic acid) and poly(ε-lysine) can be prepared by γ-irradiation. These microbial poly(amino acid)s are water soluble, hydrodegradable and biodegradable [19]. Free radical polymerization of different vinyl monomers and aniline onto gum ghatti (Gg) under dissimilar reaction conditions was also described [18]. Polyaniline (PANI) is an attractive conductive polymer because of its simple methods of synthesis, high stability, variable structure as well as unique optical, magnetic, electrical, electrochemical and electromechanical properties. To optimize their properties, reaction parameters such as synthesis time, kind of solvent, pH, microwave power, cross-linker amount, aniline concentration, initiator concentration, monomer concentration and the percentage swelling can be varied. Both radiation and thermal cross-linking methods are inexpensive, safe, do not require a purification step and result in sterile hydrogels if a suitable combination of hydrophilic polymers is used. There are numerous papers and reviews focused on the synthesis of hydrogels [20].

3. Methods of hydrogels investigation

Fourier transform infrared analysis (FTIR) can be used for the analysis of the hydrogel structure, type of the functional groups, different stages of biodegradation, crystallization deformation of polymers, moisture uptake properties, to characterize the attached biomolecules, nature of interactions between components, etc. [21–23]. In FTIR-ATR (attenuated total reflection) spectroscopy technique, a beam of infrared light is passed through the ATR crystal in such a way that it reflects at least once off the internal surface in contact with the sample (a denser medium—crystal of diamond, include germanium, KRS-5 and zinc selenide or silicon, characterized by the high refractive index and a rarer medium in the form of the thin film of sample) must be in contact with each other. This reflection forms the evanescent wave which extends into the sample. This method is used for both solid and liquid samples analysis. For

example, in the case of chitosan (CS), itaconic acid (IA) and methacrylic acid (MAA) hydrogels the characteristic bands are associated with the N–H and –OH stretching vibrations as well as those connected with the absorption process of Zn(II) were distinguished. It was also found that the stretching vibrations connected with the carboxylic groups (C=O) are weaker after absorption of Zn(II) and the strong absorption band at 1712 cm^{-1} shifted to the lower wave number 1705 cm^{-1}. The absorption band at 1540 cm^{-1}, assigned to the ionic interactions between CS and the acids, and the absorption band at 1165 cm^{-1}, assigned to the deformation absorption bands of –OH groups, were enhanced and shifted to higher wave numbers after Zn(II) absorption. On the basis of the FTIR spectra of unloaded and loaded hydrogels, it seems that $-NH_2$, –OH and –COOH groups are involved in Zn(II) ion bonding. This confirms the fact that the dominant type of bonding onto hydrogel is through chemical interactions because a signal corresponding to –COO anion is observed [24].

Atomic force microscopy (AFM) can be used for evaluation of the surface topography of hydrogels and changes in the surface chemical composition after polymerization, absorption and interaction with active agents. Grains of various sizes randomly aggregated can be seen. Another consequence of the agglomeration is the appearance of very large grains, displacement of which leaves huge holes behind.

The X-ray diffraction (XRD) method allows to determine the plane of the network and to calculate the size of the crystallographic cell. Tests are also carried out by small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) as well as differential scanning calorimetry (DSC). Differential scanning calorimetry is a technique by which the difference between the temperature of the sample and the reference samples is measured. It can be used to determine the glass-transition temperatures (T_g). The glass transition temperature is different for each polymer, but many polymers are above T_g at room temperature. The glass transition of a polymer is related to the thermal energy required to allow changes in the conformation of the molecules at a microscopic level, and above T_g there is sufficient thermal energy for these changes to occur. However, the transition is not a sharp one, nor it is thermodynamically well defined. Therefore, T_g depends on the polymer architecture and there are several factors influencing the transition: chain length, chain flexibility, side groups, branching, cross-linking, complexation. It was found that in the case of polymer metal complexes T_g and the decomposition temperature increase. For example, the decomposition temperature for the polymer complex of Cu(II) is 280°C and the T_g is about 140°C. This is the evidence that the thermal stability is enhanced by the incorporation of metal into the organic backbone. In addition, the T_g variation of metal incorporated polymer depends on the amount of metal ions and cross-linking effect of polymers. Based on the thermogravimetric analysis (TGA), the mechanism of decomposition of hydrogels can also be illustrated. The initial minor weight loss occurs due to the removal of moisture and volatile components; however, the maximum weight loss occurs due to the elimination of side chains, degradation of backbone polymer or breakdown of the cross-linked structure. Maximum weight loss observed after the first stage of decomposition of cross-linked samples indicates the chemical modification of hydrogels. In many cases, the results obtained from the TGA method and scanning electron microscopy (SEM) are consistent as for improvement of thermal stability after grafting and cross-linking.

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In the case of scanning electron microscopy (SEM), the electron beam, being the collimated stream of accelerated electrons, is focused by magnetic lenses. In the case of the emission scanning electron microscope, the electron beam with a diameter of 10–50 nm is used. As for the tunnel scanning microscope, the current flow between the soda and the test material due to the tunnelling effect is recorded while the field scanning microscope records changes in the electric field. The radiation, passing through the material reflected by its surface or dispersed, contains information about the structure and after being synchronized with the incident beam is used to obtain an image. The images obtained from a scanning electron microscope make it possible to analyze the 3D structure of the test materials at a magnification from 20 to 100,000 times. Using the SEM method, change in surface morphology due to the formation of covalent bonds between different polymeric chains, structure of the material and its porosity as well as cross-linking can be observed. Interior morphology of synthesized hydrogels can be examined by the cross-sectional SEM analysis. For example, in the paper by Sato et al. [15], the surface of macroporous hydrogels in the form of less than 1 mm sliced was analyzed using a stereo-microscope. As for the SEM analysis, the swollen samples were freeze-dried to avoid shrinkage in the drying process and frozen using liquid nitrogen. Then, they were dried under reduced pressure and coated with platinum and palladium. The hydrogels have different morphologies depending on the synthesis process. Some of them have an interconnecting, 3D porous structure, whereas others have a rather irregular structure with very large completely empty spaces.

As for quasi-elastic light scattering (QELS), a monochromatic laser radiation is used. Beam of monochromatic laser radiation is reflected from the sample surface and forms a plurality of coherent elementary waves coming from different microscopic surface features. As a result of the interference of the waves, so-called interference fringes with different intensities are formed. Water microdroplets contained in the hydrogel material result in additional waves by reflection from the surface of the incident light.

Water retention behaviour and hydrodegradation of hydrogels is very important especially with regard to the difficulties of treating hydrogels waste by existing methods due to the inclusion of substantial amount of absorbed water [19]. Hydrolytic degradation studies of hydrogels can be determined at varying temperatures up to 100°C. After placing in a deionized water, the hydrogel samples were heated and filtered. The amount of gel dissolved in water can be measured using the total organic carbon analyser (TOC method). The degradation ratio can be calculated from the ratio of filtered TOC amount to the total TOC amount of gel. For example, it was that hydrogels were not degraded when held at 40°C for 3 h. When the medium temperature was raised to 100°C, the gel was degraded to 90% during 1 h. In the case of 60 and 80°C, the rates of degradation were increased (40 and 20% of hydrogel was degraded). This was due to the fact that the density of the polymer network decreased because of scission of the polymer main chain and the removal amount of degraded polymer increased.

3.1. Mechanical properties

Examination of cross-linking and mechanical strength (compressibility at break) is based on the measurement of the maximum clamping force, the change in solubility of the polymer in

time using the compression testers. Typically, hydrogel samples are cut into cubes. The sample was placed on the sample plate of the compression tester. The compression plunger fell at a rate of 1 mm/5 s to compress the sample. For hydrogels, the compressive strength increased with the increasing concentration of monomer and the decrease in the γ-irradiation dose as well as with the decrease in the specific water content [19, 22, 23]. The hydrogels exhibited higher compressive strength in the case of higher monomer concentration or greater irradiation dose. This indicates that a higher cross-linked density causes a higher compressive strength of hydrogel. The cross-linking is connected with the swelling (P_s). It changes with temperature, pH and ionic strength.

4. Application

According to the Global Industry Analysts, Inc. report, the world demand for superabsorbent polymers will reach up to 1.9 million metric tons in the next years. The fast increase in demand will be seen on the developing markets and in new applications [25, 26]. Water-soluble polymers such as poly(acrylic acid), poly(vinyl alcohol), poly(vinylpyrrolidone), poly(ethylene glycol), polyacrylamide and some polysaccharides are the most common systems used to form hydrogels [27–31]. These water-soluble polymers are nontoxic. Their physicochemical properties such as good stability both in the swelling environment and during storage, re-wetting capability, good absorption ability (maximum equilibrium swelling), good rate of absorption, particle size and porosity, neutral pH, colourless, odourless, photo stability, low soluble content and residual monomer and non-toxicity, maximum biodegradability without formation of toxic groups and finally low price make them suitable for different applications [32, 33]. Among others, the most important are agriculture, drug delivery, sealing, coal dewatering, artificial snow production, food additives, pharmaceuticals, microfluidic control, biomedical applications, tissue engineering and regenerative medicines, diagnostics, biomimetic, biosensor/bioactuator, bioseparation and artificial skin and muscles, wound dressing, separation of biomolecules or cells and barrier materials to regulate biological adhesions and biosensor.

It should be mentioned that it is not possible to produce hydrogels with all these features, although some properties can be achieved such as porosity, response to either pH or temperature, for example, the lowest re-wetting, the highest absorption rate and the lowest residual monomer should characterize those used in drug delivery and production of personal hygiene agents [34–37]. In the case of pH-responsive hydrogels (anionic or cationic), they should contain groups that can accept or donate protons as response to pH change. Anionic hydrogels possess carboxylic or sulfonic groups and deprotonation occurs at pH greater than pK_a which causes their ionization. This, in turn, increases hydrogel swelling. Cationic hydrogels contain amine groups. In this case, ionization occurs at pH below the pK_b and increased swelling is observed. It was found that concentration, ionic charge, value of pK_a or pK_b, type of active groups, hydrophilicity or hydrophobicity, degree of ionization of both hydrogel and solution are very important. As for temperature-dependent hydrogels, their ability to swell and shrink when the temperature changes is detected. When the temperature is below the upper critical

solution temperature, hydrogels contract and release solvents from the matrix and the dehydration process takes place. At temperatures higher than that the opposite process (swelling) is observed. In the group of positive temperature hydrogels those based on copolymer of polyacrylamide and *n*-butyl methacrylate (AAm-co-BMA) as well as derivatives of chitosan are found [27]. The group of negative temperature hydrogels contains those with two hydrophilic (−CONH−) and hydrophobic (R) parts.

4.1. Agriculture and horticulture industry

Recently, the research on the use of superabsorbents as water management materials for agricultural and horticultural applications has attracted great attention. In the case of agriculture, the main role of hydrogels is release of nutrients into soil. Hydrogels can be impregnated by fertilizer components (e.g., soluble phosphate, potassium ions, nitrogen compounds). Chemicals trapped in a polymer network cannot be immediately washed out by water, but gradually released into the soil and then absorbed by plants. The simplest way to use superabsorbents in agriculture is their mixing with the soil. Introduction of cross-linked hydrogels into the root zone of plants releases not only mineral fertilizers but also pesticides. In this way, they are used in the United States per year for 400,000 hectares of crops. For this aim, polyacrylamide, poly(acrylic acid) or polymethacrylic and their derivatives, much less frequently, cross-linked poly(vinyl alcohol) and chemically modified polymers based on polysaccharides, such as chitosan, pectin and carboxymethyl cellulose, have been used [5, 38–46]. However, the use of the latest is considerably limited due to their rapid biodegradability in soil [47]. Superabsorbents increase water capacity of the soil, at the same time counteracting the loss through seepage and evaporation [48–50]. They counteract rapid changes in soil moisture acting as buffer water. They also block channels for water loss from the soil surface. The effectiveness of the process depends on the soil properties such as aeration, temperature and nutrient transport, water uptake and transformation, which affect plant growth. Therefore, applicability of cellulose-based hydrogels can be recommended for the controlled release of water and nutrients in arid and desert areas. The main advantage is controlled release of water, long time maintaining soil humidity, increase of soil porosity and therefore better oxygenation of plant roots. It was confirmed that the amount of moisture retained in the soil is dependent on the concentration of the cellulose-based superabsorbent matrices. The advantages of this type of hydrogels are also eco-friendly sources, high holding capacity, low cost and biodegradability. Moreover, their application helps reduce irrigation water consumption, causes lower death rate of plants, improves fertilizer retention in soil and increases plant growth rate [51–54].

As for slow release fertilizers combined with superabsorbents to obtain both slow-release and water retention properties are well described in the literature. In general, fertilizers and superabsorbents are combined by two methods. In the first method, fertilizers are blended with superabsorbents. In the second approach, fertilizers are added to the reaction mixture and polymerized *in situ* whereby they are entrapped in the superabsorbents. These two methods always result in a higher release rate [55, 56].

Hydrogels are also used in the cultivation of nursery plants. Superabsorbents allow to reduce the costs associated with maintaining plants, increase the survival rate of planted crops and allow for non-invasive protect seedlings of various kinds of vaccines aimed at ensuring better development of plants [54].

Hydrogels as components of horticultural substrates increase the soli water capacity. During irrigation or rainfall they bind water in the soil, preventing it from seeping into deeper layers. As a result, water is continuously provided to plants limiting water stress in plants [55–57]. It should be mentioned that further research is needed because most of the superabsorbents are based on pure poly(methacrylate) and therefore they are too expensive and not suitable for saline containing water and soils. Non-ionic polymers have a much lower absorption, but they are also less sensitive to ions in the water. Due to that many authors propose introducing inorganic clays, such as kaolin, bentonite, montmorillonite, etc., into pure polymeric superabsorbents in order to improve swelling property, hydrogel strengths and reduce production costs [58–61].

Hydrogels can also be used as a carrier of pesticides. For example, chitosan is characterized by antimicrobial and insecticidal properties. In the mixture with other active substances, it can be used as a matrix to carry bioinsecticides designed to control, for example, proliferation of insect larvae. Similarly, microcapsules of alginate and chitosan were prepared, characterized and evaluated as a carrier system for imidacloprid, synthetic analogs of brassinosteroids and diosgenin derivatives, azadirachtin, etc. Bionanocomposite materials based on chitosan as well as chitosan and clay blends (with montmorillonite) can be used as absorbents for herbicides [57, 58].

4.2. Food production and packaging industry

According to the Food and Agricultural Organization of the United Nations (FAO), increase of the global population to 9.1 billion by 2050 will be connected with the increase of the world food production by 70% and double food production in the developing world [62–64]. The application of hydrogels provides both economic and environment benefits by avoiding contamination of the ground water. Due to using too much fertilizers, water supplies are polluted. It may also lead to eutrophication, a situation where there is not enough oxygen dissolved in the water for aquatic organisms to survive. The use of coated fertilizers is a promising alternative to improve many aspects of fertilization based on the concept of controlled release. The main advantages of using controlled release hydrogels are regular and continuous delivery of nutrients, low-frequency fertilizer application and elimination of damage to roots due to high salt concentrations [65–67].

Effective food production is an integral part of food storages. Development of the concept of long-term food storage is connected with using polymers of various chemical compositions and structures. Along with the required performance properties, such as chemical durability, physicomechanical and technological properties, polymer materials used in direct contact with foods should also meet high hygienic requirements. For this aim, typical synthetic polymers as well as biopolymers widespread in nature in the form of cellulose, starch, natural rubber, silk and various resins have been used. Besides a polymer binder, plasticizers, fillers, dyes,

pore formers, lubricating agents and other components are made of these components. The most popular way to obtain degradable blends is mixing natural and synthetic polymers or incorporating inorganic fillers [68–70]. Hydrogels can also be applied to produce efficient biopolymer packaging materials with desirable properties. Stiff and rigid linear polysaccharides mixed with proteins tend to form gels in the form of sheets, membranes and coatings [71]. Several biopolymers such as starch, cellulose, chitosan, poly(lactic acid) (PLA), poly(caprolactone) (PCL), poly(hydroxybutyrate) (PHB) are used for packaging purposes. The current trend in food packaging is the use of blends of different biopolymers such as starch-PLA blends and starch-PCL blends. More globular and flexible polysaccharides form spherical structures [26]. Promising applications of hydrogels in food packaging industries include improved packaging (gas and moisture barriers), antibacterial packaging, product condition monitoring, nanoadditives, enhanced shelf life, protection from oxidation and task masking.

4.3. Biomedical applications

For the first time, poly-2-hydroxyethylmethacrylate (PHEMA) as a synthetic biocompatible hydrogel was used for contact lens applications in 1960. Hard contact lenses are primarily based on hydrophobic materials such as poly(methyl methacrylate) (PMMA) or poly(hexafluoroisopropyl methacrylate) (HFIM), whereas soft lenses are based on hydrogels. Nowadays many attempts are made to obtain lenses with good oxygen permeability. To this aim, the hydrophilic monomers: 4-t-butyl,2-hydroxycyclohexyl methacrylate, methacryloylamino-4-t-butyl-2-hydroxycyclohexane and 4-t-butyl,2-hydroxycyclopentyl methacrylate with HEMA and N-vinyl-2-pyrrolidone (NVP) are proposed [72].

Hydrogels are widely used in wounds treatment. Large wounds lead to the risk of infection and loss of large amounts of fluids. It was proved that chitosan hydrogels and their derivatives accelerate the division of fibroblasts and production of cytokines. The amount of collagen in wounds treated with chitosan materials is lower, therefore the growth of tissues does not occur so fast and the formation of small scars is observed. Chitosan is hypoallergenic and has natural antibacterial properties, which further support its use in field bandages [73, 74].

Bandages were introduced by HemCon, Inc., which develops market technologies to control severe bleeding for traumatic skin and organ injuries. Unlike the gauze, bandages made from chitosan hydrogels interact with the blood cells (chitosan molecules carry positive charge). All our cells, our blood cells, the outer membranes have negative charges. The negative charge of the blood cells is attracted by the positive charge of the chitosan. As soon as they touch each other, they fuse and form a tight, adherent clot on the surface of the wound. HemCon® bandages are conveniently packaged, stable at room temperature and simple to use. Being extremely robust and flexible, they can be used on irregular wound surfaces. They are also non-heat-producing and can easily be removed by the water. The other examples are Granugel® (ConvaTec), Intrasite Gel® (Smith & Nephew), Purilon Gel®(Coloplast), Aquaflo (Covidien) or Woundtab® (First Water) [14].

Applications involving cell immobilization in alginate hydrogels to obtain artificial organs are also very important. Hydrogels stimulate behaviour of human organs and they are sensitive to the changes of conditions such as pH, temperature, enzymes and electric field. The fact that

they are hydrophilic in nature because of reactive groups such as −OH, −COOH, $-NH_2$, $-CONH_2$, $-SO_3H$ allows them to absorb or retain large quantities of water as well as to contain bioactive materials within their network. They could be used in controlled release systems without the need to remove them due to their biocompatibility. Therefore, development of pH-sensitive biodegradable and biocompatible hydrogels based on polysaccharides, polypeptides and proteins is observed. For example, polysaccharides/polyaniline based graft-copolymers have demonstrated their potential to be efficiently used for various biomedical applications as medical implants, prosthetic muscles or organs, diagnostic devices to artificial muscles, stabilization of bone implants and decreasing thrombosis [75, 76]. Used for production of urinary catheters, they prevent bacterial colonization on the surface and provide a smooth and slippery surface to improve its biocompatibility. One of the advanced applications of hydrogels was proposed by Caló and Khutoryanskiy [14]. Hydrogels can be used to convert electrochemical stimuli into mechanical work, i.e., reversible contraction and relaxation under physicochemical stimuli for the development of artificial muscles, which function like the human muscle and tissue but with an electrically driven muscle. Hydrogels obtained from natural polymers such as agarose due to its biocompatibility and the mild conditions of gelation make them suitable for applications in tissue engineering.

Hydrogels are also applied for insulin regulation in diabetes, treatment of hemophilia B, kidney failure (urea removal), liver failure, interferon production, treatment of Parkinson disease, hypocalcemia and chronic pain [77–79].

4.4. Hydrogels in cancer treatment

Advances in chemotherapy have resulted in development of many innovative drug delivery hydrogels which have significantly improved prognosis and quality of life in cancer patients. Peppas et al. [80] and Nguyen et al. [81] reported the PEG–PLGA graft copolymeric hydrogels application for cancer treatment and cancer imaging using light-sensitive polymers with stimuli sensitive properties for potential biomedical applications. Kanamala et al. [82] indicate that pH-sensitive hydrogels for tumour-targeted drug delivery have provided a new strategy for addressing the limitations of the conventional chemotherapy, i.e., HPMA polymer-coated liposomes to target tumour extracelluar pH_{ex}. Casolaro et al. [83] synthesized and studied two acrylic hydrogels as a biomaterial to load and release the chemotherapeutic agent cis-platin. Dual stimuli-responsive hydrogel has improved the release of platinum(II)-species for the chemotherapy of solid tumours.

The most interesting approach to treatment of pancreatic cancer has been proposed by David et al. [84]. Pancreatic cancer is a deadly form of neoplasm with the highest level of mortality among different cancers. They have developed a novel material by combination of quercetin and 5-fluororacil loaded on chitosan nanoparticles. The dual drug-loaded carrier system exhibited significant toxicity towards pancreatic cancer cells in both two-dimensional (2D) and 3D cultures.

In the case of congenital anomalies, traumatic injuries or tumour resections both biocompatible carriers and specific substances for bone reconstruction are applied. Many techniques applying tissue engineering are reported to promote osteogenesis with appropriate scaffolds for bone

regeneration. Fujioka-Kobayashi et al. [85] created a drug delivery system that allows the controlled release of proteins—cholesterol-group- and acryloyl-group-bearing pullulan (CHPOA) nanogels. They were aggregated to form fast degradable hydrogels (CHPOA/hydrogels) by cross-linking with thiol-bearing polyethylene glycol. Two distinct growth factors, BMP2 and recombinant human fibroblast growth factor 18 (FGF18), were applied to a critical-size skull bone defect for bone repair by the CHPOA/hydrogel system. The CHPOA/hydrogel system can successfully deliver two different proteins to the bone defect to induce effective bone repair. The combination of the CHPOA/hydrogel system with the growth factors FGF18 and BMP2 might be a step towards efficient bone tissue engineering.

4.5. Heavy metal ions removal

In the case of heavy metal ions removal, different physicochemical properties of hydrogels can be taken into account [86–91]. Hydrogels (with and without magnetic properties) based on natural polysaccharides for Cd(II) removal from aqueous solutions were described in [92]. The chitosan-based hydrogels were synthesized with the addition of known amounts of chitosan, acrylic acid, and methylene-bisacrylamide in the presence of initiator in the form of ammonium persulfate and magnetite nanoparticles. It was found that the sorption process varies when magnetite is added during the synthesis of hydrogels. As for the contact time, pH, initial hydrogel mass and initial concentration of Cd(II) ions, it was found that the hydrogels without magnetic properties can be applied in the treatment of water and industrial effluents contaminated with Cd(II) more efficiently than those with magnetic properties. Application of new pH-sensitive chitosan-based hydrogel as a sorbent for Zn(II) ions from synthetic wastewater solutions was described in the paper by Milosavljević et al. [93]. The influence of different variables such as pH, temperature, contact time and initial concentration on the Zn(II) ions uptake was examined. The absorbate concentration (4.6, 9.2 and 14.1 mg/L), pH, absorption time (0.5–48 h) and temperature (25, 37 and 45°C) were varied. It was found that the maximum absorption of Zn(II) ions occurred at pH 5.5. The value obtained for maximum sorption capacity of 105.5 mg/g at 25°C. The hydrogel can be regenerated with 0.01 mol/L HNO_3.

The absorption of Cu(II) ions from aqueous solutions onto poly(acrylic acid-co-acrylamide) hydrogels prepared via free-radical solution polymerization was investigated by Orozco-Guareño et al. [94]. They found that hydrogel with a less cross-linking agent showed the highest capacity towards Cu(II) 121 mg/g. The effect of solution pH on the process effectiveness without dissolving of hydrogels was not observed. The Cu(II) absorption kinetics results showed that equilibrium was attained within 30 min. The absorption equilibrium data were better fitted by the Langmuir isotherm model. However, the effect of the amount of cross-linking agent was reflected in a poor fit of this isotherm equation attributed to the narrower interchain space. It was proposed that Cu(II) ions were coordinated through the carboxylic and amide functional groups to form a tetradentate surface copper complex [94].

4.6. Dyes removal

Hydrogels based on (meth)acrylates have been used in cationic dye removal, for example, (poly(methacrylic acid)-graft-cellulose/bentonite), poly(methacrylate-acrylic acid-vinyl

acetate) and chitosan-graft-poly(acrylic acid) for methylene blue removal; poly(acrylic acid-acrylamide), semi-IPN of poly(acrylic acid-acrylamide-methacrylate) and amylase and poly(glycidylmethacrylate)-graft-cross-linked acrylate based resin for crystal violet, yellow 28 (BY28) removal [95–97]. Positive values of enthalpy, negative of entropy reveal favourable, spontaneous, endothermic processes. The Langmuir and Freundlich sorption isotherms are found to describe the experimental data best. Maximal sorption capacities corresponding to the complete monolayer coverage reached 102 mg/g and 157 mg/g for poly(methacrylic acid) based hydrogels with the neutralization degrees of monomer of 0 and 80%, respectively. Also the guar gum-based hydrogels such as guar gum-acrylic acid (Gg-AA) based cross-linked hydrogels were interpenetrated with PANI and evaluated for conductivity, antibacterial properties and dye absorption application [98].

5. Perspectives

Increasing knowledge about hybrid or composite hydrogel materials allows to design very useful shape-memory and self-healing, stimuli-responsive hydrogel materials. This is a consequence of the approach wherein minimally invasive treatments are needed. At the forefront are these which determine the immediate change from a low viscous solution before injection and quick formation of a strong network *in situ* requires careful selection of appropriate cross-linkers, possibilities to modulate release and degradation profiles after hydrogel administration, shielding pharmaceutical drugs in micro- and nanoparticles, etc. Such materials are also very interesting as sorbents because during the swelling process the network structure tends to be more extensive which allows access of various molecules to active centres. It should be mentioned that they can be readily and completely regenerated without no significant change of their properties.

5.1. Electroconductive hydrogels and biosensors

Electroconductive hydrogels are polymeric blends or conetworks that combine integrally conductive electroactive polymers (CEPs) with hydrated hydrogels. Electroconductive hydrogels belong to the class of multifunctional smart materials which combine the properties of constituent materials to give rise to technologically relevant properties for devices and systems as a biorecognition membrane layer in various biosensors. As an example, the biosensors of poly(HEMA)-based hydrogel and poly(aniline) (PANI) with the incorporated recombinant cytochrome P450-2D6 and poly(HEMA)] as well as polypyrrole (PPy) hydrogels with the incorporated analyte-specific enzyme can be mentioned. Such polymers have potential applications in bioactive electrode coatings and electrochemical devices.

5.2. Indicators

pH-sensitive hydrogels can be applied in modern analytical methods such as dispersive solid-phase extraction (DSPE) also known as QuEChERS (quick, easy, cheap, effective, rugged and safe), semisolid-liquid dispersive microextraction (SSLDM), dispersive liquid-liquid microex-

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traction (DLLME) and solid-phase extraction (SPE) which are often applied for multi-residue analysis of active substances, plant extracts, pesticides etc. In many cases, some of them are free from organic solvents and therefore classified as a green analytical method (in this case, highly toxic, chlorinated solvent extractants are not applied). For example, pH-sensitive hydrogels were prepared from a catechol-conjugated alginate hydrogel and a pyrocatechol violet dye [98]. Chemical and mechanical stability in a wide range of pH values as well as a simple method of synthesis determine their application as visible sensors to withstand and monitor corrosive liquids (acids and bases) as well as radioactive compounds, hazardous wastes and infectious microorganisms.

6. Hydrogels in controlled release of fertilizers chelated by the biodegradable complexing agent IDS

Hydrogels found applications as slow-release fertilizers although the addition of fertilizers generally causes hydration reduction and affects their physical properties. Another aspect is the fact that most of the traditional hydrogels are polyacrylate-based products, thus not biodegradable and regarded as potential pollutants for the soil [99, 100]. Our research group has recently focused on the application of hydrogels in controlled release of fertilizes based on the biodegradable complexing agents. It was proved that the commercial hydrogels Luquasorb 1160 and Luquasorb 1280 can be used for the absorption of Cu(II), Zn(II), Mn(II), and Fe(III) complexes with the IDS [101].

It was found that the rate of absorption of the nutrients (macro- and micronutrients) by the plants depends not only on plant age but also on the form in which the element is supplied and the solution concentration. Micronutrients are applied in the form of simple complexes or chelates. Several compounds are used as the complexing agents. They can be both natural and synthetic. In this group, citric, formic, ascorbic, propionic, tartaric, succinic, lactic, gluconic and salicylic acids or their K, Na and NH_4^+ salts, lignosulfonates, natural and synthetic amino acids (glycine, cysteine, and glutamine), ethylenediaminetetraacetic can be listed. For example, citric acid is a natural biodegradable chelator. Because of its carboxyl groups, citric acid complexes are not stable in the acidic environment. EDTA forms strong water-soluble chelates with polyvalent metal ions over a fairly wide range of pH [102].

Liquid fertilizers applied for feeding of plants should be characterized by defined properties such as an appropriate content and ratio of macro- to micronutrients. In addition, the ligand of the sequestering agent should undergo a metabolic conversion or biodegradation. Therefore, in the present paper the new complexing agent for binding nutrient ions was proposed. ISD is characterized by excellent biodegradability.

This new, biodegradable complexing agent also known as Baypure CX 100 (Laxness, Germany) or tetrasodium salt of (*N*-1,2-dicarboxyethyl)-D,L-aspartate acid. Iminodisuccinic acid belongs to the group of biodegradable complexing agents of a new generation. It is environmentally friendly and non-toxic. It is prepared by thermal polymerization of aspartic acid and characterized by extremely rapid biodegradation, which equals approximately 80% after just

7 days [103–105]. It can solubilize in water at any ratio. Its ability to form soluble complexes with metal ions dissolved in water is in the range from 4 to 10. Formation of IDS complexes with metal ions can be described as follows (Eq. (1)):

$$M^{2+} + H_n ids^{n-4} \rightarrow \left[M\left(H_n ids\right) \right]^{n-2} \quad (1)$$

where *ids* is the ligand iminodisuccinic, *M* is the metal ion, *n* = 0–3. IDS is a pentadentate complexing agent. It forms chelates of octahedral structure with many metal ions. For example, for Cu(II) ion there are known the following complexes: $[Cu(Hids)]^{-}$, $[Cu(ids)]^{2-})]^{-}$, $[Cu(OH)(ids)]^{3-}$. The stability constants of metal complexes with IDS were presented in [106, 107]. In our previous paper [108], the influence of chemical conditions on hydrogel, kinetic and absorption behaviour towards Cu(II), Zn(II), Mn(II) and Fe(III) ions in the presence of the chelating agent of a new generation, i.e., IDS was studied. The studies were carried out to investigate the effect of the sorbent dose, pH of the solution, initial concentration as well as phase contact time and temperature on the absorption efficiency. The kinetic parameters based on the kinetic models, i.e., the pseudo first order (PFO), the pseudo second order (PSO) and the intraparticle diffusion (IPD) equations were also determined. From the linear dependence of the Langmuir and Freundlich isotherms, the maximal absorption capacities and the constants of the studied hydrogel in relation to the complexes of Cu(II), Zn(II), Mn(II) and Fe(III) with IDS were determined. Now the new hydrogels such as TerraHydrogel®Aqua, THA (Terra, Poland), Agro® hydrogel, AH (EverChem, Poland) and Zeba® hydrogel, ZH (Agrecol, Poland) were investigated. Their physicochemical properties are listed in **Table 2**.

Superabsorbent	**TerraHydrogel®Aqua (THA)**	**Agro® hydrogel (AH)**	**Zeba® hydrogel (ZH)**
Matrix	Cross-linked polyacrylate	Cross-linked acrylamide polyacrylate	Cross-linked polyacrylate
Form	Anionic	Anionic	Anionic
Commercial form	Na^+	K^+	n.a.
Appearance	White granules	White powder	White-yellow granules
The water absorbency	180–300 g H_2O/g	380 g H_2O/g	n.a.
Bead size (mm)	0.177–0.255	0.300–1.000	n.a.
Operating pH range	6–8	5–9	5–9

Abbreviation: n.a., not available.

Table 2. The physicochemical properties of THA, AH and ZH hydrogels.

In the first stage of investigations, the moisture retention capability (Q_{H2O}%) at time *t* was measured. To determine the water absorption capacity of the hydrogels, a gravimetric method was applied. It was found Q_{H2O}% values were changed from 34 to 89% for THA after the measured time intervals [104]. For AH and ZH hydrogels, they were as follows: from 25 to 73% and from 12 to 87%, respectively (**Figure 1**).

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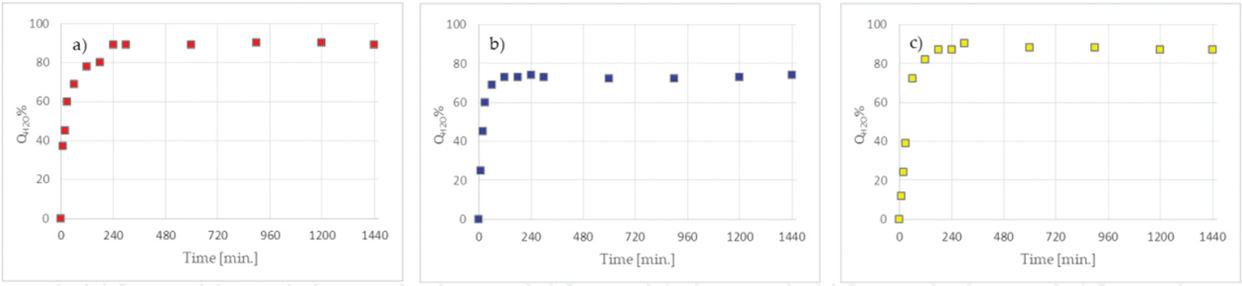


Figure 1. Comparison of water absorption capacity Q_{H2O}% of the (a) THA, (b) AH and (c) ZH hydrogels.

In the next stage THA, AH and ZH hydrogels were immersed in NaCl solution (initial concentrations in the range 0.2–1.5 M) at room temperature to reach the swelling equilibrium. After 24 h time, the samples were separated from the solution by filtration. The NaCl solution (Q_{NaCl}%) absorbency of THA, AH and ZH hydrogels were determined by weighing the swollen and dry samples. All the experiments were carried out three times to obtain the average values. It was found that Q_{NaCl}% values were equal to 10, 8 and 15% for 1.5 M NaCl solution, respectively. The obtained results were presented in **Figure 2**.

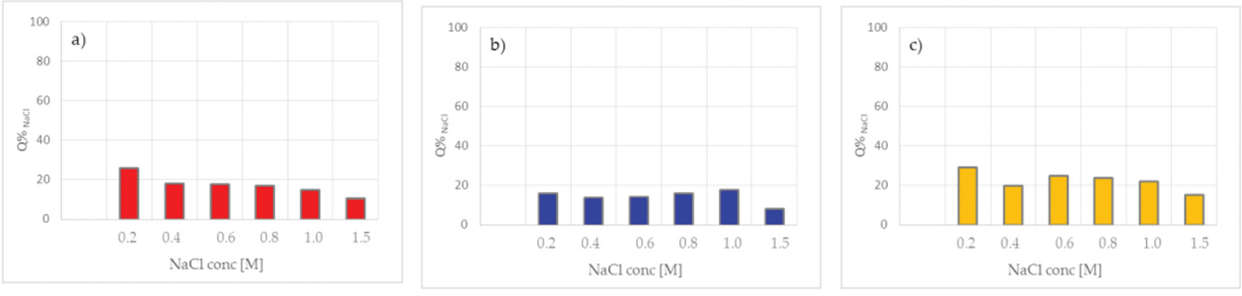


Figure 2. Comparison of NaCl absorption capacity Q_{NaCl}% of the (a) THA, (b) AH and (c) ZH hydrogels.

After immersing in water and NaCl solutions, the polymer network of negative charged due to the presence of carboxylic groups can absorb and retain a large volume of water or salt solutions. As follows from the literature data [25, 109] the rate of solution transport can be much lower than the relaxation of the polymer chains (Fickian diffusion) or diffusion is very rapid compared with the relaxation process (the rate of water movement is determined by relaxation) as well as in the intermediate case the diffusion and relaxation rates are comparable. Those estimations can be based on the equation (Eq. (2))

$$m_t / m_\infty = kt^n \tag{2}$$

where m_t is the mass of water absorbed at time t, m_∞ is the mass of water or NaCl solution absorbed at equilibrium, $k$is a characteristic constant of the polymer and n is a diffusional exponent. For $n < 0.5$, the rate of solution transport is dominated by a Fickian diffusion

mechanism, for $n > 0.5$ the dynamic swelling of the polymers is the main factor. In the case of $n = 0$, the mass transfer is independent of time.

The maximum quantity of water absorbed by THA is 190 g/g for distilled water and 119 g/g for 1.5 M NaCl solution during its 1st hydration cycle (**Figure 1**). For AH hydrogel, these values are as follows: 165 g/g for distilled water and 98 g/g for 1.5 M NaCl solution, for ZH hydrogel they are the lowest: 131 g/g for distilled water and 72 g/g for 1.5 M NaCl solution. The absorption of water by AH, ZH and THA hydrogels was found to be faster in distilled water compared to NaCl. Comparing the obtained results replicated in three steps, it was proved that the first step of hydration was the fastest (data not presented). Swelling of polymer in the case of salt solutions is smaller due to the difference in the osmotic pressure.

Static (batch) tests of absorption of metal complexes with IDS were made by putting 0.1 g of THA, AH and ZH hydrogels and 50 cm^3 of Cu(II) complexes with IDS solution (in the system M(II):IDS = 1:1) into the 100 cm^3 conical flask and shaking mechanically using the laboratory shaker for 1–120 min. The procedure was repeated three times. The samples were shaken using the laboratory shaker type 357 (Elpin Plus). The stirring speed was 180 rpm. The pH was measured using a pH meter CPI-505 (Elmetron, Poland). The concentration of Cu(II) complexes with IDS in the filtrate was determined using the inductively coupled plasma optical emission spectrometer ICP-OES of type 720 ES (Varian, Australia).

The amount of Cu(II) complexes with IDS absorbed on THA, AH and ZH hydrogels was calculated from the difference between the initial concentration and the equilibrium one. The rate of complexes absorption is expressed as percentage of the amount of metal ions absorbed after a certain time related to that required for the state of equilibrium. This can be described as follows (Eq. (3)):

$$S\% = \left(c_0 - c_e\right) / c_0 \times 100\% \tag{3}$$

The absorption capacity (qe_e, mg/g) of THA, AH, ZH hydroirst-order kinetic equation is represented as (Eq. (4):

$$q_e = \left(c_0 - c_e\right) / m_d \times V \tag{4}$$

where c_0 is the initial concentration of M(II) complexes with IDS solution (mg/dm^3), c_t is the concentration of M(II/III) complexes with IDS in the aqueous phase at time t (mg/dm^3), V is the volume of the solution (dm^3) and m_d the mass of the dried hydrogel (g). The examplary results of sorption of the Cu(II)-IDS complexes on THA are presented in **Figures 3** and **4**.

The data show that the amount of Cu(II) ions sorbed by THA hydrogel increases with the increasing of concentration the complexes. The absorption percentage (S%) also increases with increasing concentration. For the Cu(II)-IDS complexes at the concentration 100 mg/dm^3, the equilibrium time was attained in 10 min, whereas equilibrium was reached in about 20 min for the concentration 200 mg/dm^3 and 1 h for 300 mg/dm^3.

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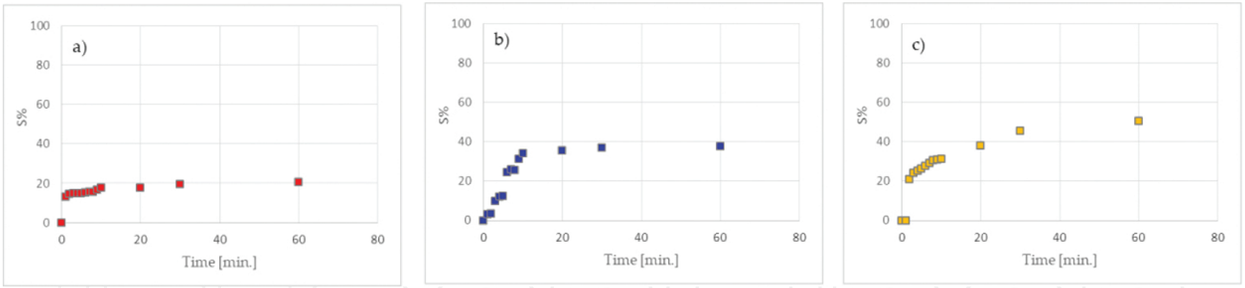


Figure 3. Comparison of *S*% of Cu(II) ions in the presence of IDS at different initial concentrations: (a) 100 mg/dm^3, (b) 200 mg/dm^3 and (c) 300 mg/dm^3 on THA hydrogel (0.1 g of THA, 250–500 μm, 100 cm^3 of Cu(II)-IDS solution, pH 6, 298 K).

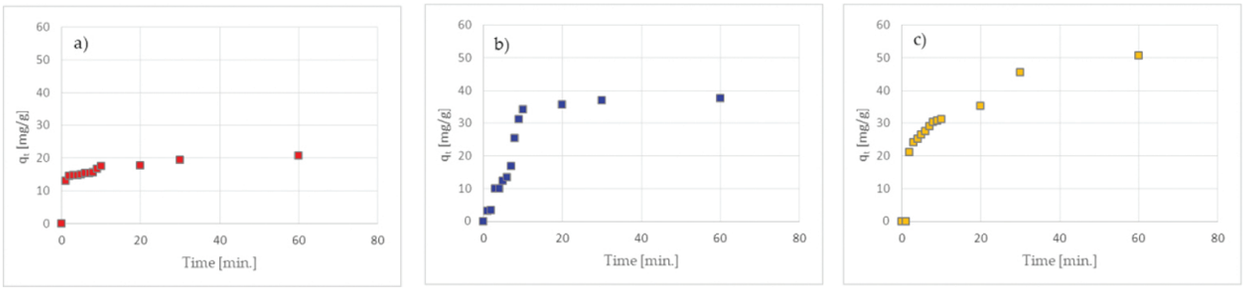


Figure 4. Comparison of absorption kinetics of Cu(II) ions in the presence of IDS at different initial concentrations: (a) 100 mg/dm^3, (b) 200 mg/dm^3 and (c) 300 mg/dm^3 on THA hydrogel (0.1 g of THA, 250–500 μm, 100 cm^3 of Cu(II)-IDS solution, pH 6, 298 K).

For estimation of kinetic parameters the pseudo first order (PFO) and the second order kinetic (PSO) models were used [110, 111]. The pseudo first-order kinetic equation is represented as (Eq. (5))

$$\log\left(q_e - q_t\right) = \log q_e - \left(k_1 t / 2.303\right) \tag{5}$$

where q_e and q_t denote the amount of absorption at equilibrium and at time t (mg/g), respectively; k_1 is the rate constant of the pseudo first order absorption (1/min). Based on the plot of log $(q_e - q_t)$ vs. t the kinetic parameters were calculated. The pseudo second-order model is expressed as (Eq. (6))

$$t / \mathrm{q}_t = \left(t / q_e\right) + 1 / k_2 q_e^2 \tag{6}$$

where q_e and q_t denote the amount of absorption at equilibrium and at time t (mg/g), respectively; k_2 is the rate constant of the pseudo second-order absorption (g/mg min). The kinetic parameters were calculated based on the plots of t/q_t vs. t. Comparisons of absorption

kinetics of Cu(II) ions in the presence of IDS at different initial concentrations on the THA hydrogel fitted by the pseudo first and pseudo second kinetic models are presented in **Figures 5** and **6**.

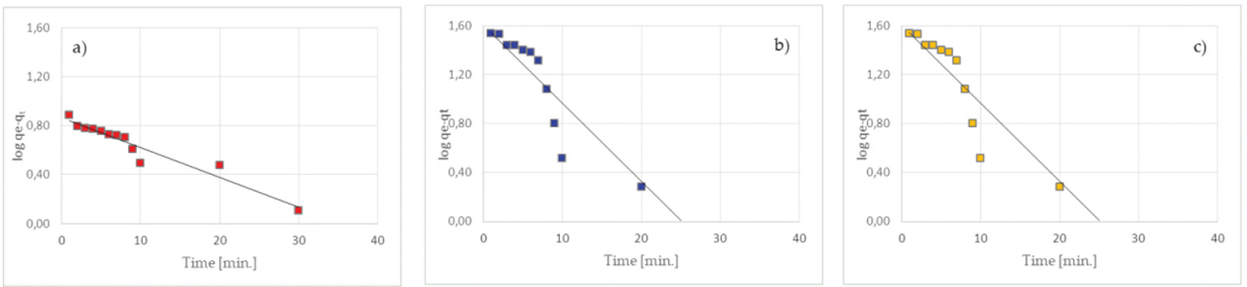


Figure 5. Comparison of absorption kinetics of Cu(II) ions in the presence of IDS at different initial concentrations: (a) 100 mg/dm^3, (b) 200 mg/dm^3 and (c) 300 mg/dm^3 on the THA hydrogel fitted by the pseudo first kinetic model (0.1 g of THA, 250–500 μm, 100 cm^3 of a Cu(II)-IDS solution, pH 6, 298 K).

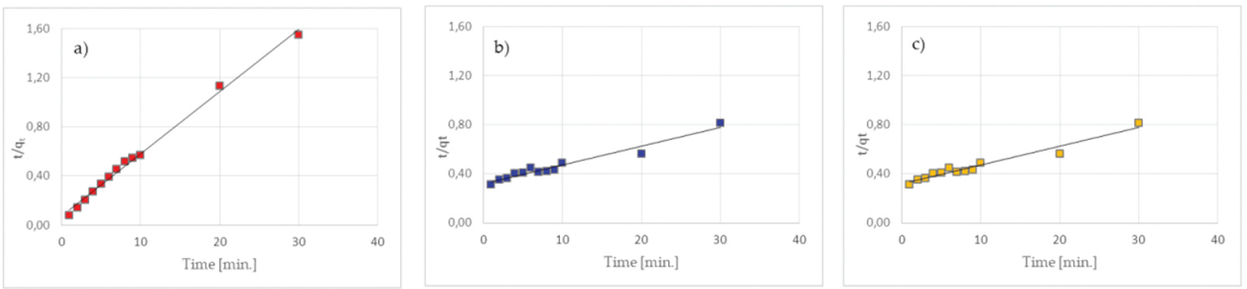


Figure 6. Comparison of absorption kinetics of Cu(II) ions in the presence of IDS at different initial concentrations on THA hydrogel fitted by the pseudo second kinetic model (0.1 g of THA, 250–500 μm, 100 cm^3 of Cu(II)-IDS solution, pH 6, 298 K).

The determined kinetic parameters of the process indicate that its course is consistent with the reaction mechanism typical of the pseudo second-order reaction in the case of Cu(II) complexes sorption with IDS as confirmed by high values of the correlation coefficients and the calculated sorption capacities are in the agreement with the experimental data. The kinetic sorption data were better fitted with the use of the pseudo second kinetic model, which yielded the best correlation coefficients R^2(>0.99) and the rate constant k_2 in the range 0.002–0.035 for the Cu(II)-IDS complexes. The obtained data also show that the k_2 rate constant decreased with the increase of the initial Cu(II)–IDS concentration, which confirmed that the time to reach sorption equilibrium increased with the initial concentration.

Furthermore, the experimental data were analyzed according to the Weber-Morris kinetic (Eq. (7)), i.e., the intraparticle diffusion model (IPD) given below [112]:

$$q_t = k_i t^{1/2} + C \tag{7}$$

where k_i is the intraparticle diffusion rate constant (mg/g min$^{0.5}$), C is the intercept which reflects the boundary layer effect.

The comparison of absorption kinetics of Cu(II) ions in the presence of IDS at different initial concentrations on the THA hydrogel fitted by the pseudo first and pseudo second kinetic as well as Weber-Morris models are presented in **Figures 5** and **7**.

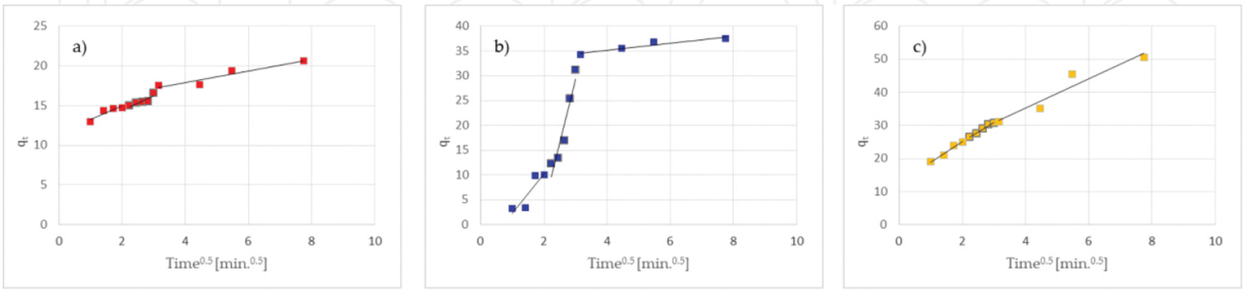


Figure 7. Comparison of absorption kinetics of Cu(II) ions in the presence of IDS at different initial concentrations on THA hydrogel fitted by the intraparticle diffusion model (0.1 g of THA, 250–500 μm, 100 cm^3 of Cu(II)-IDS solution, pH 6, 298 K).

It was also observed that the absorption process can be divided into three stages where the slope corresponds to the absorption rate. In the first stage, the regression line with short intercepts almost passed through the origin, suggesting that the intraparticle diffusion is not the sole rate controlling step. The sharper slope was attributed to the diffusion of studied complexes to the external surface of hydrogels or the boundary diffusion layer. The second stage implied the gradual absorption, where intra-particle diffusion was rate-controlling. As the contact time increases, the effect exerted by the external mass transfer in absorption rate-controlling becomes more and more evident. The intraparticle diffusion slowed down in the third stage due to low concentration of Cu(II)-IDS complexes. It can be concluded that intraparticle diffusion plays a predominant role in the first stage of the sorption process.

THA, AH and ZH hydrogels were also characterized by the pH of the point of zero charge pH_{zpc} determination using the pH drift method. Their pH in 0.01 M NaCl solution was adjusted between 2 and 12 by adding 0.1 M NaOH and 0.1 M HCl. 0.2 g of the THA, AZ and ZH was added to 50 cm^3 of the solution and after 24 h the final pH was measured. As follows from the previous studies pH_{zpc} determined for the THA hydrogel was equal to 6.9 [104]. For AZ and ZH hydrogels those values were equal 7.4 and 6.5. At pH > pH_{zpc} the surface charge will be negative while at pH < pH_{zpc} positive and therefore pH affects the sorption process. In the whole pH range of 2–11, THA was the most efficient for removal of Cu(II)-IDS complexes. Generally, the absorption is more favourable at the pH values 4–10 and decreases at the pH values of 2 and 13. The analogous results were obtained for AH and ZH hydrogels. However, a slight loss of the mass of the used hydrogels was observed. Therefore to examine stability (mass loss) of the used hydrogels, the samples were immersed at room temperature in buffer solutions at pH 1.96, 4.01, 7.0, 9.0 and 11.0 for 3 h. Mass loss was determined by the gravimetric method, as previously. It was found that at pH 11 the mass loss was the largest

and equal to 36 and 24% for AZ and ZH hydrogels, respectively. It can be noticed that the swelling ratio of the hydrogels increases at pH greater than 1.96 and decreases sharply for the samples at pH 11.0. At pH 1.96, H-bonding between −OH, −CO and −COOH groups increases the cross-linking density and hence results in small swelling ratio, especially for AH hydrogel. At pH 7.0, the carboxylic groups are dissociated and the hydrogen bonds are disrupted. The electrostatic repulsion between the polymer chains occurs and THA, AH and ZH hydrogels tend to swell. At pH greater than 7.0, the polymeric chains swell rapidly and deprotonation of the basic groups and dissociation of the acidic groups carboxylic groups occurs.

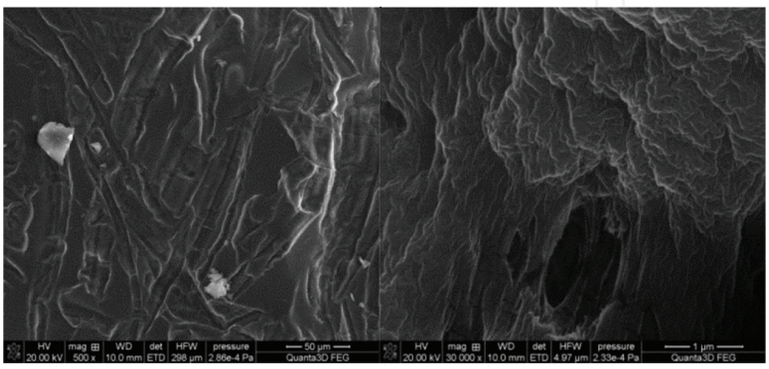


Figure 8. SEM scans of THA before the sorption of Cu(II)–IDS complexes.

For the used hydrogels, scanning electron microscopy images were also recorded using Quanta 3D FEG microscope (FEI). Fourier transform infrared spectra of THA were obtained using the attenuated total reflectance technique (FTIR-ATR) and measured with a FTIR Carry 630 spectrometer (Agilent Technologies). The bands at 3400 cm^{-1} (ν_{as} NH_2), 3190 cm^{-1} (ν_s NH_2) and 1687 cm^{-1} (C=O) are characteristic of the acrylamide unit. The characteristic stretching 2 vibrations at 1453 cm^{-1} connected with the presence of $–CH_2$ group as well as the symmetric and asymmetric stretching vibrations of the carboxylate ion (COO^{-1}) at 1399 and 1553 cm^{-1} are also visible [113, 114].

It should be mentioned that the samples were prepared before the sorption process (**Figure 8**).

7. Conclusions

Cross-linked hydrophilic polymers are capable of absorbing large volumes of waters and salt solutions. Therefore, they can find widespread applications in bioengineering, biomedicine, food industry and water purification as well as in separation processes. They are also applied in the production of slow release of fertilizers. In the present paper, the application of the biodegradable complexing agent, iminodisiccinic acid (IDS) for the sorption of Cu(II), was presented using commercially available hydrogels. It was found that with the increasing phase contact time and concentration the sorption effectiveness increases. The equilibrium state is established at the phase contact time about 10–20 min depending on the complex concentration

of the initial solution. The determined kinetic parameters of the process indicate that its course is consistent with the reaction mechanism typical of the pseudo second-order reaction in the case of sorption Cu(II) complexes with IDS as confirmed by high values of the correlation coefficients and the calculated sorption capacities are in the agreement with the experimental data. TerraHydrogel®Aqua, THA hydrogel can find application in the controlled release of fertilizers based on the biodegradable complexing agent.

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