Obtaining swelling hydrogels to improve fertility and the benefit of retaining sandy soils

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Abstract. The article provides information on the preparation of polyelectrolytes and swelling polymeric hydrogels with different specified properties. The analysis of domestic and foreign scientific literatures is presented. Particular attention of researchers is paid to rare cross-linked polyelectrolytes, the so-called supermoisture absorbents or hydrogels. Thanks to a complex of variable unique properties, supermoisture absorbents have found the widest application on the world market in medicine, industry, agriculture, and in solving water and environmental problems.

1 Introduction

Solving the problems of integrated rational use of natural resources (water) and environmental protection is a key task for the sustainable socio-economic development of Uzbekistan. The main reasons for the complex ecological shutdown in the region are the low effectiveness of the use of water and land resources, irrigation and drainage systems, and the relatively weak implementation of scientific and technological achievements in various sectors of the national economy.

In this regard, the solution of the problem of water balance in the Republic of Uzbekistan is an urgent task. It requires the implementation of the necessary measures, the most important of which include soil improvement techniques aimed at increasing the effectiveness of irrigated and sustainable rainfed agriculture, the development of methods to combat wind and erosion, desertification and other negative phenomena associated with the exploitation of lands in the arid zone.

A relatively new direction in this area is the creation of swellable polymer hydrogels, as a promising means of improving the water regime of light pores, mainly sandy ones, as well as plant welfare.

Hydrogels have a complex of interesting properties such as good ion exchange and membrane activity, the ability to reversibly swell multiple times in water, strong physical, mechanical and protective characteristics, as well as the ability to undergo chemical and physical modification. Such a variety of properties is due to the peculiarities of the chemical structure of hydrogel macromolecules, ion-exchange and absorption-active

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abilities, selectivity of ion exchange, depending on the degree of development of the macronetwork structure, as well as the ability to accumulate and proactively consume exchange-bound water for a long time.

Hydrogels adsorb up to several thousand grams of water per gram of dry polymer and change their volume and morphology. Due to such unique properties, hydrogels can be used as supermoisture absorbents, specific and exchangers, etc. In addition, hydrogels are very promising as regulators of the properties of various technological disperse systems.

2 Results and discussion

2.1 Preparation and properties of polymer hydrogels

Among the huge number of known natural and synthetic polymers of substances, only a few can dissolve in water. Water-soluble polymers are characterized by the presence of hydrophilic functional groups (hydroxyl, carboxyl, amide, sulfo, etc.) in the chain of macromolecules. Many of them belong to the class of polyelectrolytes [1]. Water-soluble polymers and hydrogels are valuable products that have the properties of polyelectrolytes.

Polyelectrolytes are polymers capable of dissociating in aqueous solutions with the formation of macromolecular ions, moreover, in one macromolecule many repetitive charge purifications occur.

It is known that all high-molecular-weight polyelectrolytes dissolve, since molecules with ionogenic groups interact with polar liquids more strongly than with non-polar ones. Synthetic polyelectrolyte is used to accelerate the filtration of various suspensions in hydrometallurgy, in the purification of industrial and waste waters, to accelerate sedimentation processes, and also as an additive to dispersed systems for the purpose of settling solid particles during the stabilization of clay suspensions and soil structure formation [2].

Due to the presence of a triple bond, the nitrile group easily undergoes many chemical transformations: reduction, addition of alcohols, saponification, etc. [3]. From a practical point of view, the saponification of nitrile groups in the chain of examples is more interesting and convenient, the mechanism of which is like the mechanism of hydrolysis of aliphatic nitriles, in which the latter are converted into amides or carboxylic acids.

Structured polyelectrolyte solutions are gels. Acrylamide-methyl-methacrylate copolymer hydrogels were obtained at various ratios of amide and acrylate units using chemical and physical crosslinkers. Physically crosslinked hydrogels were prepared by polymerization using benzoyl peroxide as the initiator, while chemically crosslinked hydrogels were prepared using N,N-methylene bisacrylamide as the crosslinker. The influence of external conditions such as temperature and pH on the swelling properties of hydrogels was investigated. The swelling temperature and pH of these gels depended on the content of acrylamide in the macromelic chain. The gels showed 21-35% swelling at 60°C, which was reversible and very stable [4].

Hydrogels based on acrylamide and potassium methacrylate were synthesized by simultaneous radical polymerization in an aqueous medium using a redox initiator ammonium persulfate and NN-tetramethylenediamine at room temperature. The degree and other characteristics of the swelling process were set. Obtaining gels had good swelling capacity, resistance to saline solutions [5]. A hydrogel based on chitosan and hydroxyethyl methacrylate has been obtained. The swelling of the gel was studied by immersing it in an aqueous solution of NaCl at various concentrations. It has been shown that the saline solution has a significant effect on the swelling of the gel [6].

Gels were obtained by polymerization of vanilimidazole in aqueous solutions of glucose oxidase. The swelling of these gels was characterized by an increase in their volume by a factor of 1800 per gram of example [7].

Gelation in aqueous solutions of cellulose ethers of polyacrylamide [8] under the action of trivalent chromium salts has been studied quite well. Gels based on these water-soluble polymers are of great practical importance; they are used in the oil industry to limit water inflow to oil-bearing layers [9].

The effect of shear fields on the rate of physical semidilute solutions of ultrahigh molecular weight surfactant in propylene carbonate, as well as on the structural features of the resulting gels, has been studied. It has been shown that at 30–70°C in a uniform shear field, with increasing shear stress, the induction period of gelation decreases from several hours to several seconds [10].

The gel was formed by adding multiply charged inorganic cations (Ca^{2+} , Cu^{2+} , Al^{3+} , etc.) to an aqueous solution of sodium alginate [11], which act as crosslinking agents, interacting with carboxyl groups of polysaccharide molecules.

It is known that coordinatively cross-linked gels are widely used in the oil and gas industry. So, according to the data, 25% of producing wells in the USA become profitable only when they are activated by hydraulic fracturing carried out using coordinate-crosslinked gels. [12].

The synthesis of water-soluble polymers has been patented by a number of foreign authors [13]. Copolymers of acrylic and methacrylic acid and alkali metal hydroxides, amines or NH₃; powdered water-soluble polymers based on acrylic and ammonium acrylate; acrylic and methacrylic acids, their amides, Na, K, and ammonium salts, as well as quaternary salts, have a spatial network structure. The spatial mesh polymer structure contains dispersion water in its cells, depriving the entire system of fluidity. From the point of view of polymer-solvent interaction, gels are divided into lyophilic and lyophobic.

To characterize polymer hydrogels, two parameters are used: the volume concentration of the polymer (A) and the degree of crosslinking (B) [14].

U. K. Akhmedov with coworkers developed a new method for the chemical modification of a copolymer of styrene and raspberry anhydride with mono- and diethanolamines in an aqueous organic medium [15, 16]. The possibility of purposeful regulation of the content of hydroxyl groups in the chain, as well as the length of side carbohydrate radicals by choosing the appropriate amidating agent, has been shown. Their physical and colloidal chemical properties have been studied, and the relationship between the surface and bulk properties of their aqueous solutions has been revealed.

A new non-toxic hydrogel material with a spongy structure has been synthesized by precipitation polymerization of hydroxyethyl methacrylate. On its basis, implants for ophthalmic reconstructive surgery were created. It was shown that the obtained endoprostheses have good compatibility with the tissues of the orbit of the eye. By the reaction of copolymerization of hydroxyethyl methacrylate with acrylamide, a material was obtained that can increase the degree of swelling in aqueous solutions, which makes it possible to create implants that increase their size in a controlled manner during operation [17].

In [18], the alkylation reactions of linear poly-5-vinyltetrazole with di- and polyfunctional compounds containing mobile halogen atoms or oxirane rings were used to obtain samples of a network polymer. In the ionized state, cross-linked poly-5 vinyltetrazole is capable of limited swelling in water to form hydrogels. It has been shown that tetrazole-containing hydrogels can serve as a matrix for stabilizing metal particles existing in the nanoscale state (Figure 1).



Figure 1. Structure of the cross-linked hydrogel.

The authors obtained swelling hydrogels based on hydrolyzed Nitron fiber with formaldehyde and polyvalent metals [19].

Thus, from the above, it follows that nitrogen-containing water-soluble polymers and hydrogels can be obtained by various methods (polymerization, polycondensation, copolymerization, polymer-analogous transformations) based on various monomers and polymers. Depending on the synthesis conditions (temperature, reagent concentration, reaction time, nature of the crosslinking agent, type of reaction), it is possible to obtain linear and crosslinked polymer structures to varying degrees, combining ionic and nonionic hydrophilic functional groups and hydrophobic hydrocarbon chains.

2.2 Chemical ameliorants of moving sands and their mechanism of action

Chemical reclamation of moving sands is their consolidation, improvement of waterphysical properties with the help of structure-forming mineral or organic substances or synthetic origin. The word "reclamation" in literal translation from Latin means "improvement". Over the past 20-30 years, sandy deserts have become an arena for the intensive development of natural resources: oil, gas, non-ferrous and rare metals, etc., the construction and operation of various engineering structures, communications, residential complexes for service personnel. Working conditions in sandy deserts are complicated by harsh climatic and environmental conditions, hot climate in summer, cold in winter, and permanent deflationary processes [20,21].

Chemical ameliorants of soils and sands are substances used to fix them and improve their properties. Currently, there is no unified classification. In [22], their conditional classification is given by origin, by type of compounds (organic, inorganic), by state of aggregation (liquid, solid), by solubility (water-soluble, water-dispersed, soluble in alkaline solutions, organically soluble); by molecular weight (low and high molecular weight); according to the chemical composition and structure of molecules (low molecular weight mineral salts, inorganic clay dispersions); according to the type of bond between the particles of the solid phase; according to the structure formed on the sand surface (crystallization, coagulation, condensation-crystallization) [28, 29].

There is a known method of fixing moving sands using oil [23]. The presence of polar groups in oil contributes to the implementation and enhancement of its adhesive interactions with sand, and its high viscosity, due to strong molecular interactions between the constituent components, favors filling the pores of the sand and slowing down its flow in the sand column.

Polymer complexes of cross-linked carboxymethyl cellulos, starch to form superabsorbent polymers and their performance as irrigation water retention aids were evaluated. The super swelling polymer has been crosslinked with aluminum sulfate octadecahydrate for optimal water retention. Starch from vegetables and chemically modified cellulose fibers have been used as the basis for the polymer structure due to their biodegradability and the sustainability of their sources. Starchy vegetables include potatoes, cassava, and corn. Radish seeds were planted in pots that contained soil with hydrogel (as well as unadjusted soil control). Plants were given a healthy amount of water for the first two weeks, then watering was reduced to see how the plants responded to drought. Unadjusted plants stopped growing after the first two weeks and showed signs of dehydration [24,25].

The use of polymers in agriculture is gaining popularity in science, especially in the field of polymer chemistry. This provided a solution to the problems of modern agriculture, which is to maximize the productivity of land and water without threatening the environment and natural resources. Superabsorbent polymer hydrogels potentially affect soil permeability, density, structure, texture, evaporation, and the rate of water penetration through soils.

Functional polymers have been used to increase the effectiveness of pesticides and herbicides, allowing lower doses to be used and indirectly protect the environment by reducing pollution and cleaning up existing pollutants. In the paper a detailed review study was compiled as a publication on the myriad applications of the polymer in agriculture, highlighting the current research trend, impact on food security, and future prospects [26,27].

Polymer matrices were prepared from hydroxyethyl cellulose and cross-linked with borax (sodium pyrobourate). Evaluation of the rate of release of new fertilizers was studied as a result of agricultural experiments. Drying of dry, fresh weight and (94) seeds was determined 30 days after planting, and then dry weight soil nitrogen content was determined also 90 days after planting. On the other hand, new polymer matrices have been used to stabilize sandy loamy soils. The effectiveness of new polymeric fertilizers as a soil stabilizer was accompanied by the determination of the diameter of aggregates mm and the average diameter (mm) of aggregates formed during soil treatment with solutions of new polymeric fertilizers [28]. Synthetic ameliorants of moving sands include low and high molecular weight surfactants of anionic, cationic, nonionic, and ampholytic types [29]. These substances, dissolving in water, lower its surface tension and have the ability to conduct electric current. Therefore, high-molecular surfactants belong to the type of polyelectrolytes. Polyelectrolytes include such polymers, in the macromolecules of which there are groups with acidic or basic properties -COONH₄; -SO₂OH; -PO(OH)₃; NH₂ NOH; CONH₂, etc. Depending on the nature of the groups, polyelectrolytes are strong or weak acids, bases or their salts. Synthetic sand ameliorants can be obtained from monomers or by processing a number of technical products, as well as from natural and synthetic polymers.

A wide range of polyelectrolytes is obtained on the basis of polyacrylonitrile by purposefully modifying it. Based on the waste fiber "nitron" type "B" and "M" by its saponification, K-9 drug was developed and introduced on an industrial scale at the Navoiazot Production Association.

According to [28-30], chemical melioration of moving sands should be attributed to surface methods of fixing. The essence of the chemical melioration of moving sands is the application of a dispersion (melt or solution) of ameliorants of chemical reagents to the surface of moving sand, resulting in a multicomponent system of the chemical reagent - dispersion medium - dispersed phase. Forces of attraction and repulsion of different nature will act between the components of this system.

In the process of evolution, plants adapted to the harsh conditions of desert life (saxaul, kandym, cherkez, etc.). Sandy soil was formed by the interaction of mineral substances of sand, plants and bacteria. Any attempts to create artificial nutrient media for growing plants ultimately rely on knowledge of the properties of any natural soils and their composition, i.e. composition of minerals that can be absorbed by plants from these soils.

The absence (or its extremely low content) in the desert sands of the soil absorbing complex, due to their constant weathering and movement, as well as the constant acute shortage of water, the most important factor in the ion exchange process, explains the low fertility of the desert.

3 Conclusion

The study shows that water-soluble polymers and swelling hydrogels, depending on the type of functional groups, relative concentration, and application conditions, play a very important role in many sectors of the national economy. Of the monomers, acrylic acid is of great importance, because. it can simultaneously or sequentially participate in various reactions, which opens up new prospects for modifying its macrochain at room temperature and obtaining products with important properties practically without energy costs.

Thus, the analysis of the literature data shows that the problem of creating water-soluble polymers and swelling hydrogels based on them for targeted regulation of the colloid-chemical properties of various disperse systems is under intensive development.

The basis for obtaining amphiphilic polymer structures for colloidal chemical purposes should be a polymer matrix that is highly soluble (or swellable) in water, in the volume of which links of hydrophilic -COONH₄, -CONH₂, -COOH and other groups should be distributed, separated by hydrocarbon regions of various lengths, allowing purposefully change the degree of ionization and intermolecular crosslinking of macromolecules.

Particular attention of researchers is paid to rare cross-linked polyelectrolytes, the socalled supermoisture absorbents or hydrogels. Thanks to a complex of variable unique properties, Supermoisture absorbents have found the widest application on the world market in medicine, industry, agriculture, and in solving water and environmental problems. However, most polymeric absorbents, having high absorption characteristics, have physical and mechanical properties that are unacceptable during operation, which significantly limits the potential for their use, for example, when creating materials of a given shape.

References

- 1. K.S. Akhmedov, *Water-soluble polymers and their interaction with disperse ones* (Tashkent: Fan, 1969)
- 2. B.P. Barabanov et al., Izvestiya of VUZ 20(24) 582-584 (1977)
- 3. E. J. Locome. Polymer sci. 24(105) 227-245 (1975)
- 4. T. Begam, Jour. Monomers and polymers 7(1) 311-330 (2004)
- 5. K. Murthy, M. Mohan, Jour. Polymer Sci. 53(1) 33-36 (2004)
- 6. J.K. Seon, R.Sh. Su, Smart materials and structures 13(5) 1036-1039 (2004)
- 7. P. Nursel, S. Bekir, G. Olgun, Journal of Biomaterial Science 16(2) 253-266 (2005)
- 8. C. Allain, L. Salome, Macromolecules 23(4) 981 (1990)
- 9. A. Pastoriza, L. Pacios, Polymer science 23(8) 1205-1211 (2005)
- 10. S.A. Udra et al., Journal of VMS 50(12) 2125-2131 (2008)
- 11. J.O. Takhirov, R.N. Turaev, Journal of Mathematical Sciences 187(1) 86-100 (2012)
- 12. J. Menjivar, Water Soluble Polymers 53(1) 33-36 (2004)
- 13. S. Moe, K. Draget, Skjak-Braek, O. Smidsrod, *Food Polysaccharides and their Applications* (New York: Marcel Dekker, 1995)
- 14. S. G. Starodubtsev, O.E. Filippova, N Journal of the Navy 34(7) 72 (1992)
- 15. U.K. Akhmedov, K.M. Adylova, Method for modifying a copolymer of styrene and Maleic anhydride Appl. No. 3471108-05 publ.22.07.82 (Open invention, 1984)
- 16. U.K. Akhmedov, K.M. Adylova, Zhurnal prik.khim Z 686-688 (1987)
- 17. L.I. Valuev, I.L. Valuev, I.V. Obydennov, Naval Forces Journal 54(5) 798-801 (2012)
- V.N. Kizhnyaev, T.L., Petrova, F.A. Pokatilov, V.I. Smirnov, VMS Journal 53(12) 2188-2195 (2011)
- 19. A.O. Asamatdinov, U.K. Akhmedov, Uzbek chemical journal of the Academy of Sciences of the Republic of Uzbekistan **3** 34-47 (2003)
- 20. N.G. Zakharov, I.B. Revut, V.L. Leontiev, V.P. Dubrovsky, L.S. Doshchenko, A new method of fixing moving sands (M., 1954)
- 21. A. Kulman, Artificial soil structure formers (Moscow: Kolos, 1982)
- 22. A.A. Baran, Polymer-containing disperse systems (Kiev: Science thought, 1986)
- 23. L. Tu, S. Schubarth, B Wolters, J. Kromer, 0il and Gas J. 90(23) 66 (1992)
- F. Nnadi, C. Brave, Journal of Soil Science and Environmental Management 2(27) 206-211 (2011)
- S.Kim, G. Lyer, A. Nadarajah, J. M. Frantz, L. Alison, International Journal of Polymer Anal. Charact. 15 307-318 (2010)
- 26. A. M. da Silva, Journal of Sustainable Development 3(24) 315-319 (2010).
- 27. O.A. EL-Hady, S.M. Shaaban, Australian Journal of Basic and Applied Sciences 6(26) 422-429 (2012)
- S. Kuldasheva, B. Jumabaev, A. Agzamkhodjayev, L. Aymirzaeva, K. Shomurodov, Journal of Chemical Technology and Metallurgy 50(3) 314-320 (2015)

- 29. N. Adizova, S. Abdurakhimov, S. Kuldasheva, I. Axmadjonov, IOP Conference Series: Earth and Environmental Science **839(4)** 042075 (2021)
- 30. T. Abdulkhaev, S Kuldasheva, G.Raximova, M.Aripova, S. Toshev, IOP Conference Series: Earth and Environmental Science **839(4)** 042074 (2021)