

PROPERTIES OF HIGHLY SWELLING HYDROGELS DERIVED FROM NATURAL COMPONENTS

Samatov S.M., Turaev Kh.Kh., *Kholnazarov B.A., Samariddinov J.T., Abdiyev B.N., Abdurakhmonov S.T., Abdullayeva N.S., Sharifova L.B.

Termez State University, Termez, Uzbekistan

*Corresponding Author: kholnazarovbakhodir@gmail.com

Abstract - The aim of this study is to synthesize a new type of biodegradable superabsorbent hydrogel, based on Carboxymethyl starch - CMS), natural minerals (zeolite, perlite, apatite), vinyl monomers (acrylic acid - AA, acrylamide AAm) and cross-linking agents N,N'-methylenebisacrylamide (MBA). The results show that the swelling capacity and water absorption time of hydrogels are affected by the concentrations of NaCl, Na₂SO₄, CaCl₂, MgSO₄, AlCl₃, CaCO₃ and NH₄Cl present in the solution. Natural minerals — zeolite, perlite and apatite— were incorporated into the hydrogel matrix to investigate their effects on the material's water absorption and moisture retention properties. The obtained samples were characterized using their morphology was examined using scanning electron microscopy (SEM). The hydrogel is designed to be cost-effective and capable of conserving water and mineral fertilizers, preventing soil erosion, salinization, and compaction, enhancing plant resistance to pests, and increasing crop productivity.

Keywords - Carboxymethyl starch, **hydrogel**, Natural minerals, **Radical polymerization**, Acrylic acid, acrylamide.

Introduction

In recent years, the development of environmentally friendly and biodegradable superabsorbent hydrogels (SAHs) has gained considerable attention due to the growing need for sustainable materials in agriculture, biomedicine, and environmental protection [1]. Conventional hydrogels based on synthetic monomers such as poly (acrylic acid) and poly(acrylamide) exhibit excellent water absorption capacity; however, their high production cost, poor biodegradability, and potential environmental hazards limit their large-scale application [2]. Therefore, the combination of natural polymers and mineral fillers has emerged as a promising strategy for designing cost-effective and eco-sustainable hydrogels with enhanced performance. Natural polysaccharides, particularly starch and its derivatives, are among the most widely used biopolymers for hydrogel synthesis owing to their abundance, renewability, and inherent biodegradability [3-4]. Corn starch, as a

representative natural polymer, provides a flexible backbone for graft copolymerization with vinyl monomers, allowing the formation of three-dimensional networks with tailored swelling and mechanical properties [5].

To further enhance the functional performance of such hydrogels, the incorporation of natural minerals as inorganic fillers has proven effective in improving mechanical stability, water retention, and environmental durability [6]. Among natural minerals, clinoptilolite, perlite, and diatomite are of particular interest due to their unique physicochemical characteristics. Clinoptilolite, a natural zeolite, exhibits high cation exchange capacity and adsorption ability, making it useful for nutrient retention and controlled release [7]. Perlite, an amorphous volcanic glass, contributes to porosity and structural integrity, whereas diatomite, composed mainly of amorphous silica, enhances the surface area and water retention potential of composite hydrogels [8]. The synergistic effect of these minerals within the polymeric network can significantly modify the swelling kinetics and stability of the resulting material. The interaction between mineral fillers and polymer chains also plays a crucial role in determining the hydrogel's water absorption behavior, particularly in saline environments [9]. Previous studies have shown that the presence of monovalent, divalent, and trivalent ions can markedly influence the degree of swelling due to ionic crosslinking or charge screening effects [10-11]. Understanding these interactions is essential for optimizing hydrogels intended for agricultural applications, where varying soil salinity and ion composition can affect performance. The obtained results demonstrate that the incorporation of natural minerals not only enhances the hydrogel's water absorption and retention capacity but also reduces production costs and improves its ecological safety, making it a promising material for sustainable agricultural applications.

Experimental part

Synthesis of the Superabsorbent Hydrogel

A highly absorbent hydrogel based on carboxymethyl starch (CMS), acrylamide (AAM), acrylic acid (AA), perlite, zeolite, and apatite was synthesized by copolymerization. Potassium persulfate (KPS) was used as an initiator to initiate the polymerization, and N,N'-methylene-bisacrylamide (MBA) was used to form spatial linkages between the polymer chains. 20 g of carboxymethyl starch was dissolved in 250 mL of distilled water using a stirrer at a temperature of 45-50°C for 60 minutes, resulting in a homogeneous solution. In the second vessel, 36 g of acrylic acid was taken and it was neutralized to 70% using potassium hydroxide. The temperature was controlled because the neutralization process was accompanied by heat release. After the resulting solution was brought to room temperature, it was added dropwise to the SMC solution and mixed. Then, 18 g of acrylamide was added and mixed until completely dissolved. Zeolite, perlite, and apatite, sized to 100 µm, were used as

mineral fillers. In this case, 8 g of zeolite, 5 g of perlite and 4 g of apatite were added. The minerals were evenly distributed in the polymer medium by mixing the mixture for 20 minutes. Then 0.4 g of potassium persulfate (KPS) was added to the system and mixed for 15 minutes. 0.3 g of N,N'-methylenebisacrylamide (MBA) was added to form a network between the polymer chains. The reaction process was carried out for 3 hours at a temperature of $60 \pm 1^\circ\text{C}$.

The IR spectrum of the synthesized CMS-g-(AA-AAm-zeolite-perlite-apatite) based highthroughput hydrogel was analyzed. The absorption region observed in the region of 3349.44 cm^{-1} corresponds to the valence vibrations of the hydroxyl ($-\text{OH}$) and amine ($-\text{NH}$) groups. This peak indicates the presence of bound water molecules in the polymer ($-\text{OH}$), amide groups of AAm, and the product. The width of the absorption regions indicates the formation of hydrogen bonds between the chains. The intense absorption around 1559.92 cm^{-1} is interpreted as being associated with the asymmetric vibrations of the carboxylate groups ($-\text{COO}^-$) in the polymer and, in part, with the deformation vibrations of the amide groups. The appearance of this peak confirms the partial neutralization of acrylic acid and its graft polymerization into the polymer network. The peak at 1403.14 cm^{-1} corresponds to the symmetric vibrations of carboxylate groups. This signal indicates the formation of acrylic acid-based polymer segments and the presence of ionized functional centers in the hydrogel. The absorption in the region of 504.43 cm^{-1} is associated with mineral components and is mainly explained by the deformation vibrations of Si-O-Si and Si-O-Al bonds in zeolite and perlite, as well as phosphate groups in apatite.

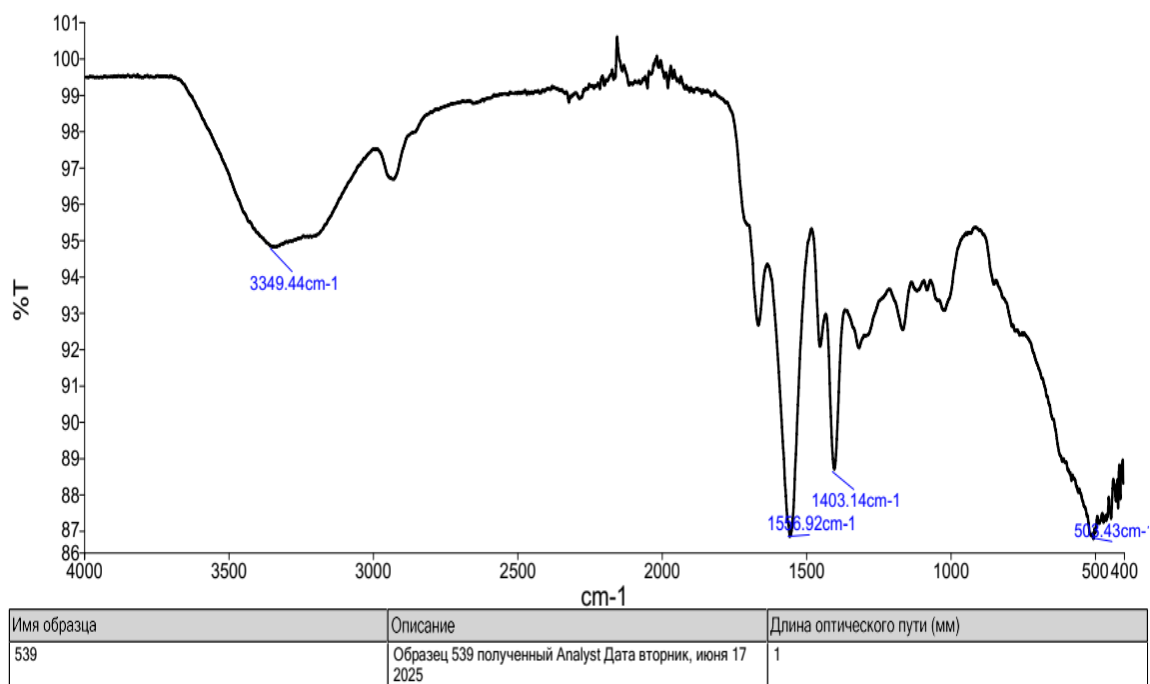


Fig. 1. IR of superabsorbent hydrogel CMS-g-(AA-AMm/zeolite, perlite, apatite)

Table 1 shows the effect of the amount of zeolite–perlite–apatite and the molar ratio of AA:AAm on the water absorption capacity of hydrogels. The experiment was carried out at the following amounts of CMS (20%), MBA (0.3%), KPS (0.7%) and reaction temperature (60 ± 1 °C). In this case, only the water absorption capacity is mainly explained by the effect of the ratio of mineral filler and monomers.

Table 1. Dependence of hydrogel water absorption on the amount of reagents.

Zeolite, perlite, apatite) %	Mole ratio of monomers AA:AAm	CMS %	MB A %	KPS %	Reaction temperat ue °C	Water absorptio n (g/g)
3/2/2	1:1	20	0,3	0,7	60±1	215
3/3/2						226
3/4/3						237
4/4/3						253
4/4/4						271
5/5/5	1:2	20	0,3	0,7	60±1	288
5/4/4						304
5/5/2						319
5/5/3						343
5/6/5						356
6/3/3	1:3	20	0,3	0,7	60±1	372
6/4/3						389
6/5/4						401
6/6/5						412
6/5/3						403
7/4/4	2:3	20	0,3	0,7	60±1	418
7/5/4						433
7/6/5						416
7/7/5						424
7/5/5						405
8/4/3	2:1	20	0,3	0,7	60±1	477
8/4/4						509
8/5/4						547
8/6/4						541
8/7/5						532

Conclusions

In this study, hydrogels with a new composition based on CMS-g-(AA-AAm/zeolite, perlite, apatite) were synthesized using the radical polymerization method. In the

process of synthesis, carboxymethyl starch was used as the main polymer matrix, acrylic acid and acrylamide as monomers forming hydrophilic functional groups, zeolite, perlite and apatite minerals served as fillers that increase the mechanical strength of the hydrogel and reduce its cost. IR analyzes confirmed the successful polymerization and the presence of interactions between the polymer matrix and the mineral particles. These properties allow them to be used in agriculture as soil moisture management, water-saving materials, and controlled fertilizer release products.

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