

Original Article

Synthesis of Superabsorbent Hydrogels Based on Starch Copolymer/Minerals Powder

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Received: 31 October 2022

Revised: 14 December 2022

Accepted: 19 December 2022

Published: 24 December 2022

Abstract - This study aims to obtain a low-cost agricultural hydrogel is containing mountain minerals based on starch copolymer. Also, the effect of mountain minerals - bentonite, kaolin and montmorillonite on water absorption of superabsorbent hydrogels was studied in the research work. During the studies, it was found that the optimal temperature of copolymerization is 65 °C, and the reaction duration is 4 hours. The water absorption of the resulting hydrogels in various concentrations of distilled water and saline solutions was determined. The effects of starch and acrylamide mole ratios, initiator, binder and mountain minerals - bentonite, montmorillonite and kaolin concentrations on the degree of swelling of the synthesized superabsorbent hydrogels were studied. It has been established that minerals added during the synthesis of hydrogels increase the water absorption of hydrogels and reduce their cost.

Keywords - Starch, Acrylamid, Macromolecular hydrogel, Crosslinking agent, Radical polymerization.

1. Introduction

A hydrogel comprises hydrophilic polymer chains connected by physical, chemical or polymerization methods [1-3]. Hydrogels can hold large amounts of water due to surface tension and capillary forces [4, 5]. Water absorption by a hydrogel depends on hydrophilic functional groups, the state of water, and the density of interconnected hydrogel networks [6-8]. The effectiveness of hydrogel properties includes biocompatibility and environmental friendliness, which makes them widely used [9,10]. Binding reagents added during the synthesis of hydrogels increase the molecular weight of hydrogels and improve water absorption and mechanical properties [11-13]. Hydrogels are commonly used in industries such as medicine, pharmaceuticals, horticulture and agriculture. [14, 15]. As for the material, hydrogel can be made from natural and synthetic polymers. Hydrogels based on natural polysaccharides are of great interest to consumers because they are biodegradable and cheap [16, 17]. To reduce the use of synthetic hydrogels in nature, it is very important to produce hydrogels based on starch copolymers. The synthesis of superabsorbent hydrogels by polymerization of a dilute solution of monomers has been studied in recent years [18-20]. The synthesis of superabsorbent hydrogels by polymerizing a dilute solution of monomers in the presence of bentonite, kaolin and montmorillonite has been studied in recent years [21, 22]. An inexpensive superabsorbent hydrogel can be obtained by polymerizing starch with acrylic amide,

bentonite, kaolin, and montmorillonite. These minerals increase the absorption properties of superabsorbent hydrogels [29, 30].

2. Materials and Methods

2.1. Materials

Potato starch (St), acrylic amid (AM) and potassium persulfate (KPS), N, N'-methylenebisacrylamide (MBA), montmorillonite, kaolin and bentonite used bentonite clay brand "Navbahor" (Uzbekistan).

2.2. Methods

2.2.1. Fourier Transform Infrared (FTIR) Analysis

The IR spectrum of the samples was obtained on a Shimadzu Fure infrared spectrometer (range 400-4000 cm⁻¹, dimensions 4 cm⁻¹) manufactured in Japan. The interactions between reagents were studied.

2.2.2. SEM Analysis

The surface morphology of the sample was studied using a scanning electron microscope (SEM-EDS-JSM-5500LV, JEOL, Ltd.). The analytical settings included a vacuum of 40 Pascals, a working distance of 8.5 mm, and an accelerating voltage of 20 KV.

2.2.3. Differential Scanning Calorimetry (DSC) Analysis

It was also studied in a Netzsch Simultaneous Analyzer STA PG 409, a differential scanning calorimeter in an inert



gas atmosphere at a nitrogen flow rate of 50 ml/min (Institute of Bioorganic Chemistry of the Federal Republic of Uzbekistan). The temperature range of the measurement is 20-390°C, and the heating rate is 5 K/min. The amount of the sample is 5 mg.

2.2.4. Water Absorption Analysis (Q)

1g of the hydrogel dried in a vacuum drying cabinet at 60 °C to a constant mass was taken and immersed in 1L of distilled water and various salt solutions for 24 hours [25, 26]. Then, the pores of the water-soaked hydrogel (M_2) were filtered through a 0.1 mm nylon mesh and held until no water remained on the surface. In this case, the water absorption capacity of the hydrogel (Qeq.g/g) was calculated according to the following equation.

$$Q_{eq} = \frac{M_2 - M_1}{M_1} \quad (1)$$

Where: Qeq (g/g) is the water absorption capacity per gram of the dry sample, M_1 is the weight of the dry sample, and M_2 (g) is the weight of the swollen sample [27, 28].

3. Experimental Part

3.1. Preparation of Superabsorbent Hydrogel

First, 162 ml of distilled water and 16.2 g of corn starch were mixed in a four-necked flask equipped with a stirrer, thermometer, condenser, and nitrogen gas. Dissolved oxygen in the solution is purged with a stream of nitrogen for 15 minutes. Then, starch gelatin was obtained at 65°C for 45 minutes under a stream of nitrogen gas. The gelatin was brought to room temperature, and 60 ml of distilled water was added to the gelatin, 14.2 g of acrylamide, 0.2%

methylenebisacrylamide (by weight of acrylamide), 0.5% potassium persulfate (by weight of starch and acrylamide), and 5 % bentonite (by weight of starch and acrylamide). Then, the reaction was carried out at a temperature of 65°C for 4 hours with stirring in an inert gas atmosphere. Then, the reaction product was ground to 0.2 mm and hydrolyzed in 1000 mL of 4% sodium hydroxide solution at 90°C for 80 minutes. The resulting product was washed with distilled water until the medium became neutral and filtered. Then the product was dried to a constant mass in a vacuum drying oven at 60°C. The yield of the obtained product was 97.8%, and it was a superabsorbent hydrogel.

4. Results and Discussion

4.1. Fourier Transmission Infrared Spectroscopy (FTIR) Analysis

The structure and functional groups of the obtained superabsorbent were analyzed by IR spectroscopy. Fig. 1 shows the spectra of superabsorbent hydrogel based on starch, acrylic amide and bentonite St-g-AM/B. The absorption line in the region of 3200.87 cm^{-1} indicates the presence of -ON and NH_2 groups, which were not involved in the synthesis reaction of the superabsorbent hydrogel containing St-g-AM/B. 2933.73 cm^{-1} spectra indicate the presence of a C-O group on the St-g-AM/B. Absorption lines in the region of 1548.84 cm^{-1} and 1403.21 cm^{-1} indicated the carboxyl groups formed after hydrolysis. Absorption lines in the region of 1660.7 cm^{-1} of the IR spectra indicate the presence of free -NH- groups. The new peak at 1447.58 and 1043.21 cm^{-1} corresponds to the -COO⁻ functional group. During the study, it was found that the characteristic absorption areas for OH and -NH₂ groups changed after the polymerization reaction.

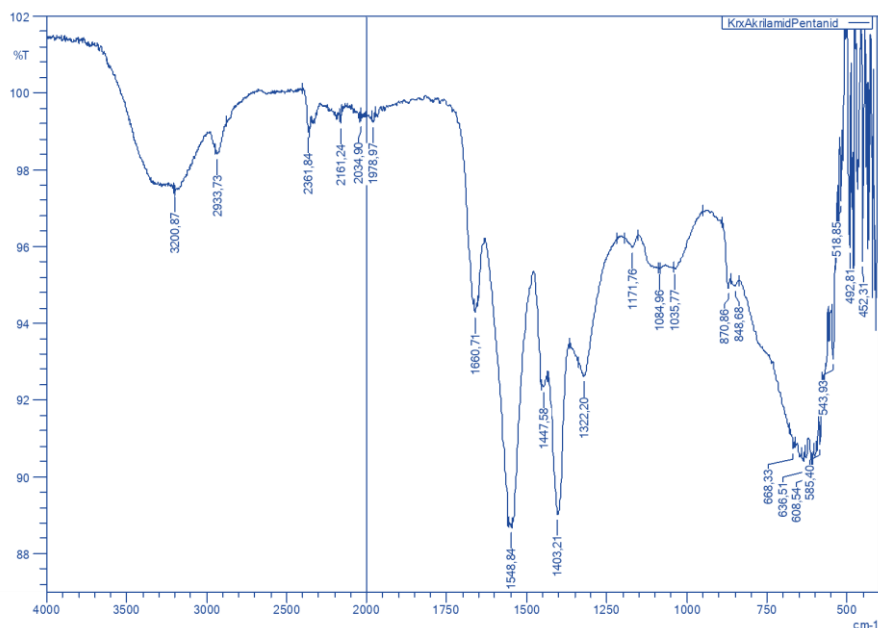


Fig. 2 IR of superabsorbent hydrogel St-g-AM/B

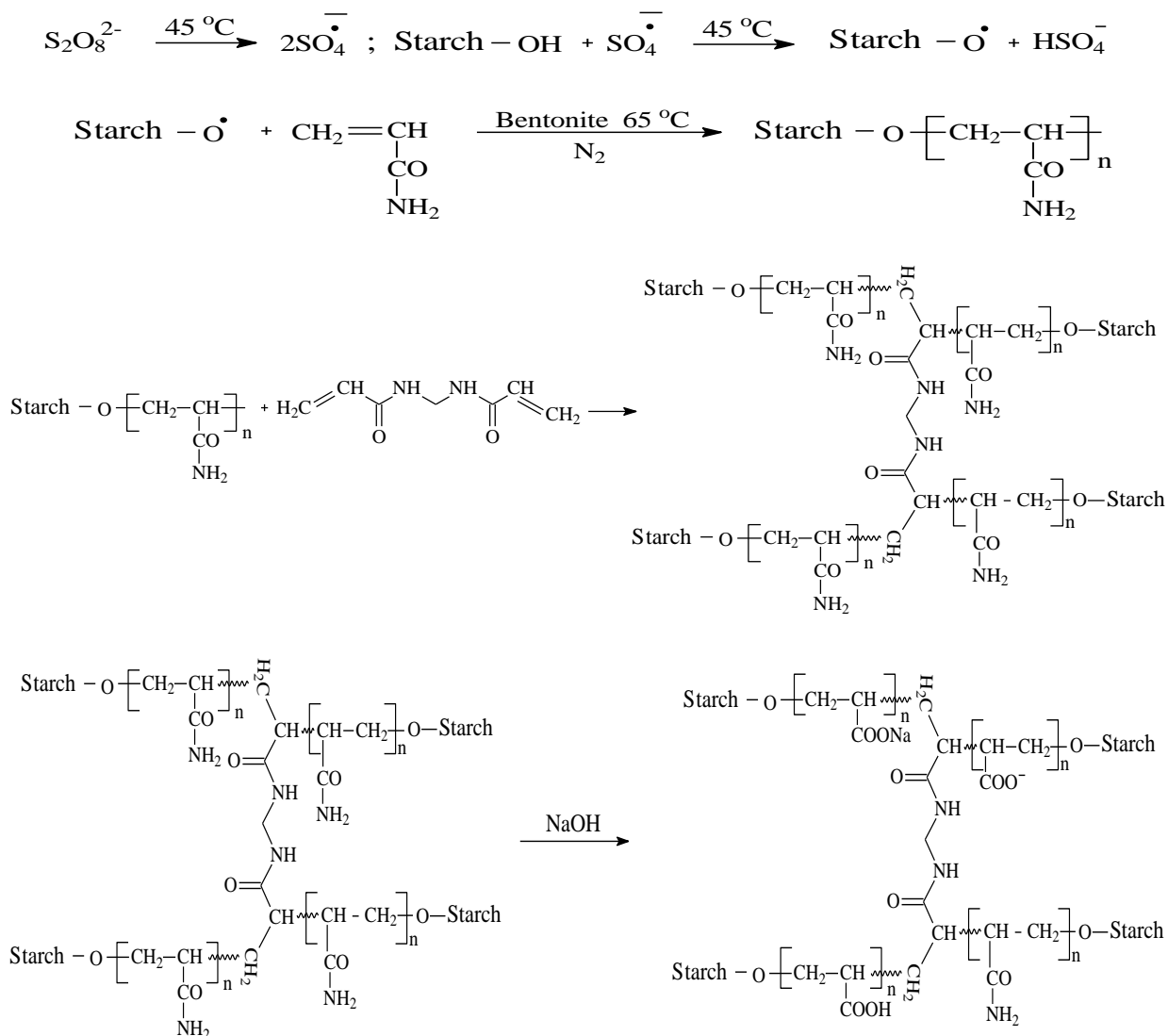


Fig. 3 Superabsorbent hydrogel preparation reactions by copolymerization of starch-acrylamide and bentonite through chemical crosslinking in the presence of MBA.

First, radical centers were formed in the initiator effect for grafting starch and acrylic amide using a binder. The crosslinked first network is a starch-acrylic amide, while methylenebisacrylamide MBA (cross-linker) crosslinked with grafted PAM chains forms the second network. It can be seen that the polymerized acrylic amide is crosslinked with the OH groups in the starch. We can also see that methylenebisacrylamide bonds with polymerized acrylamide to form a high molecular weight polymer chain.

As a result of the FTIR spectra analysis, the approximate structural formula for obtaining the St-g-AM/B superabsorbent hydrogel can be summarized by the following reactions (Fig. 3)

Fig. 4 the formation of new groups after the hydrolysis process. The unreacted component of bentonite is evenly

distributed in the polymer mass and forms porous structures. The resulting pores improve the water absorption capacity of the hydrogel and, conversely, return water when needed.

The resulting product is hydrolyzed with sodium alkali, and new lyophobic functional groups are formed. The water absorption capacity of hydrogels is due to the presence of hydrophilic groups such as OH, -CONH, -CONH₂, -COOH, -COONa, -COO⁻ along the polymer chain.

4.2. Morphology of Superabsorbent Polymer

Also, the morphology of hydrogel based on St-g-AM/B was studied by SEM analysis method. Fig. 5 it can be seen that the surface morphology of St-g-AM/B-based superabsorbent hydrogel differs from the surface morphology of starch and bentonite.

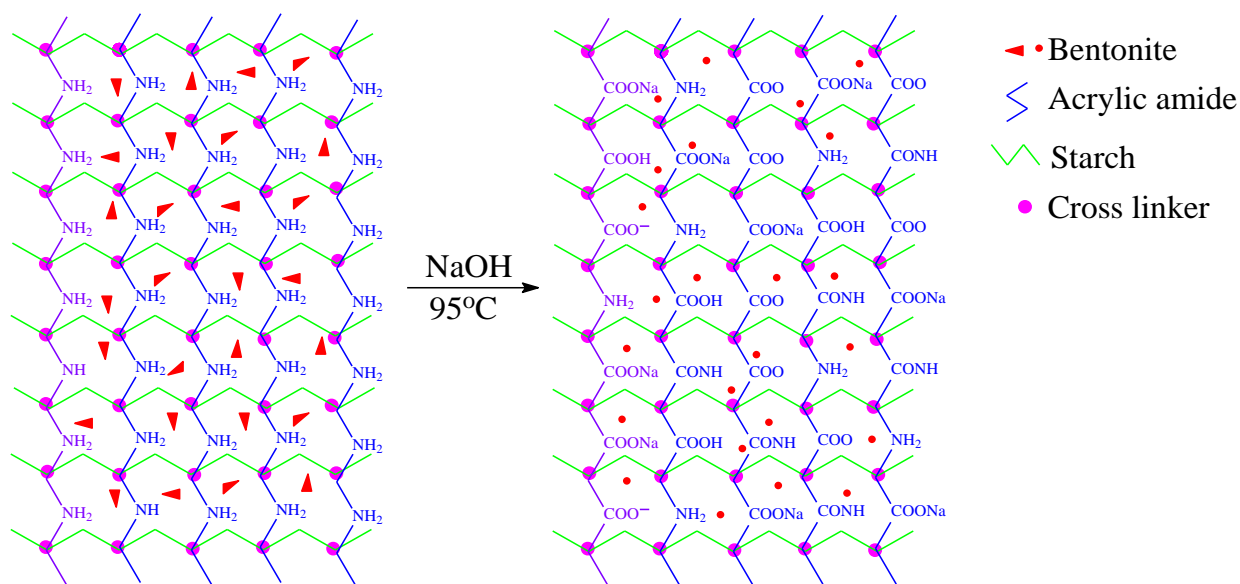


Fig. 4 Formation of new groups in the process of hydrolysis and distribution of bentonite in the product.

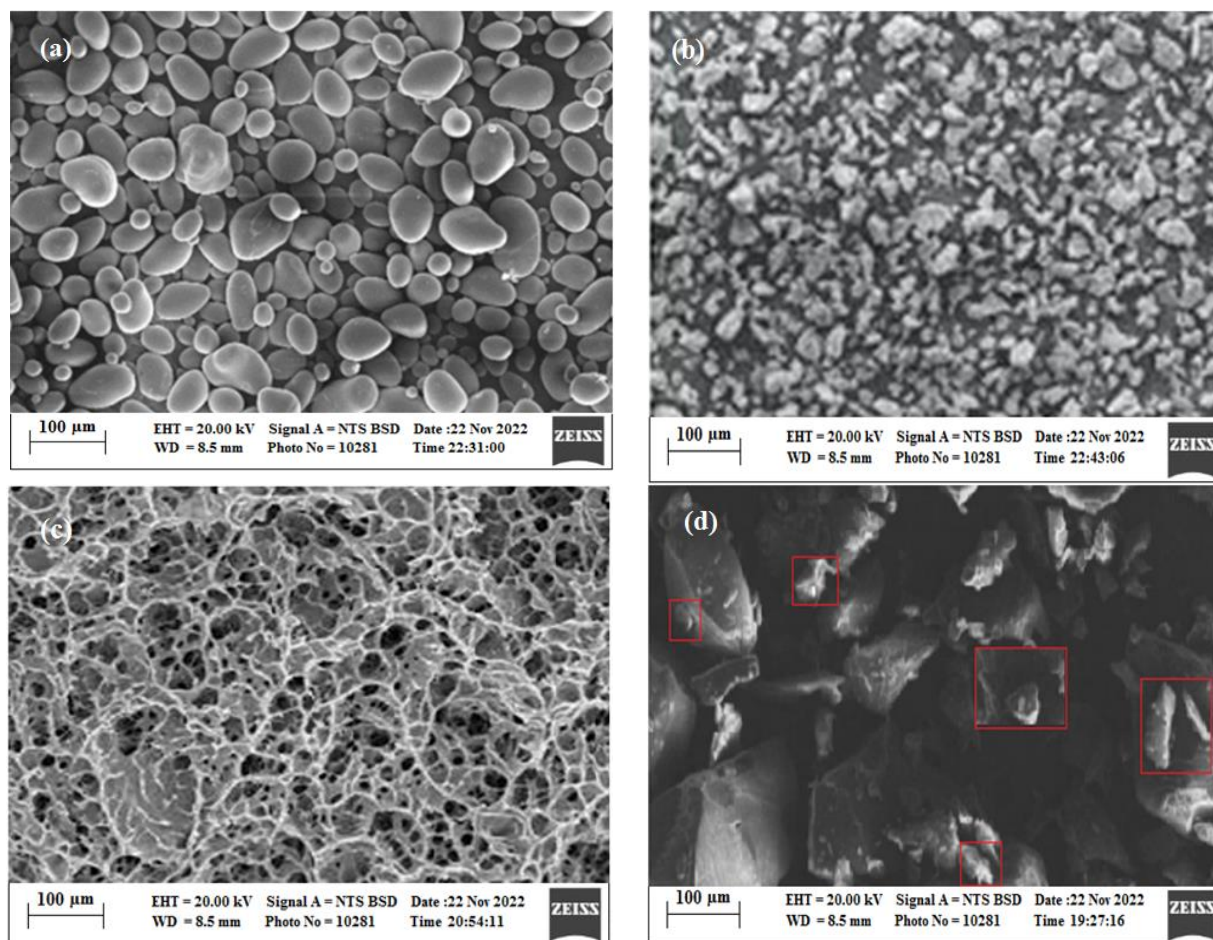


Fig. 5 Micrographs of (a) starch, (b) bentonite, (c) non-swollen hydrogel St-g-AM/B, and (d) superabsorbent hydrogel swollen in water St-g-AM/B.

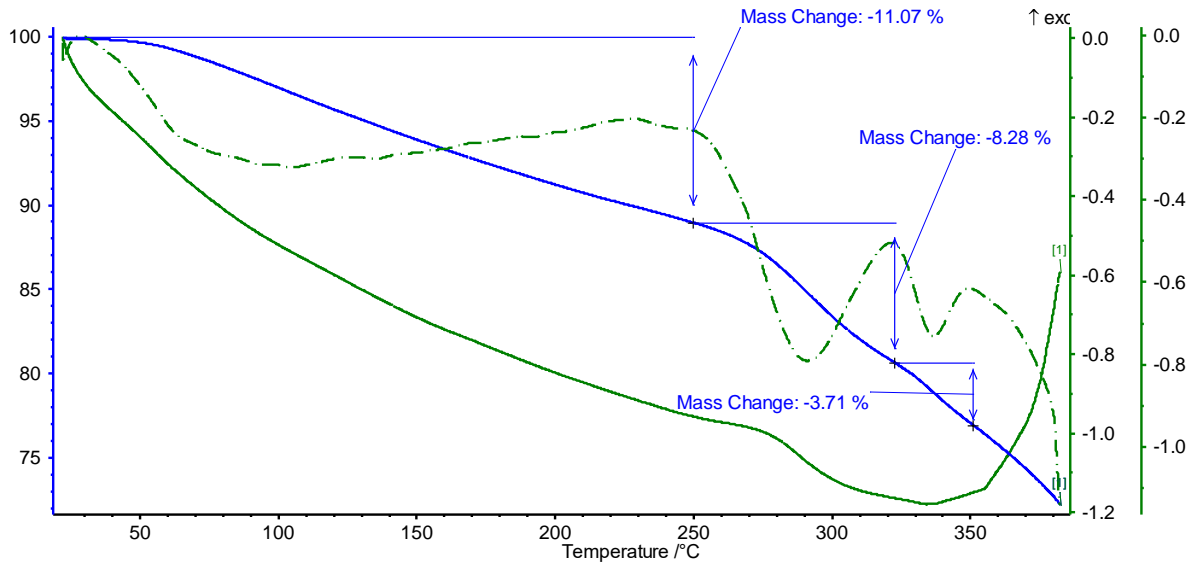


Fig. 6 Thermal analysis of superabsorbent hydrogel St-g-AM/B.

4.3. Thermal Stability of Superabsorbent Hydrogel

Fig. 6 no sharp mass loss is observed in the product. Mass loss occurs in 3 stages above 70°C, the first stage at a rate of -11.07%/min from 70-250°C, the second stage at a rate of -8.28%/min from 250-320°C, and the third at 320-350° C begins to decay with a mass loss of -3.71%/min. The first mass loss occurs due to a small amount of moisture in the hydrogel at a temperature above 70°C; the second mass loss occurs as a result of the decomposition of amino groups in the polymer at a temperature above 250°C. The third mass loss is a result of the breaking of bonds at a temperature above 320°C.

Fig. 7 shows that hydrogel swelling is high when the initiator concentration is 0.5% relative to the mass of acrylamide and starch. When the concentration of the initiator exceeds 0.5% (relative to the mass of acrylamide and starch), the active centers increase, resulting in the formation of a polymer with a low molecular weight due to the formation of irregular bonds. This leads to a decrease in hydrogel swelling.

If the concentration of the binding reagent exceeds 0.2% by weight of acrylamide, very close and dense bonds are formed, as a result of which the water absorption of the hydrogel decreases.

Fig. 8 also shows that kaolin and montmorillonite minerals were used instead of bentonite to synthesise superabsorbent hydrogels. When kaolin and montmorillonite were used instead of bentonite, water absorption of hydrogels was significantly improved. This is because kaolin and montmorillonite, unlike bentonite, are partially purified from additional oxides such as TiO₂, Fe₂O₃, MgO, Si-, Na₂O, K₂O, P₂O₅, SO₃, FeO. During the reaction, these oxides affect the binding points of the polymer chain, causing a decrease in

the molecular weight of the polymer. As a result, the water absorption of the hydrogel decreases. This can be seen in Fig. 8.

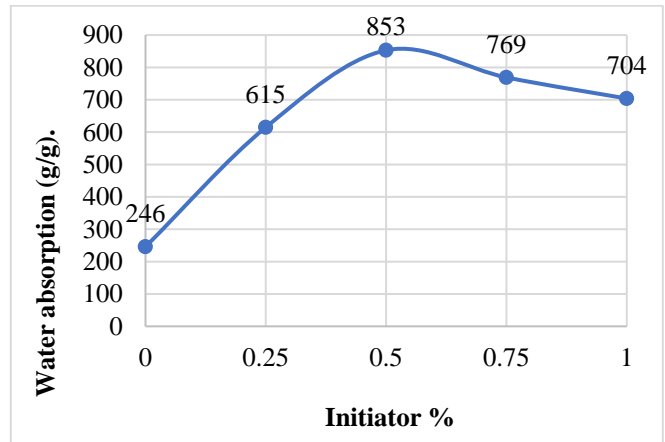


Fig. 7 Effect of initiator concentration on water absorbency

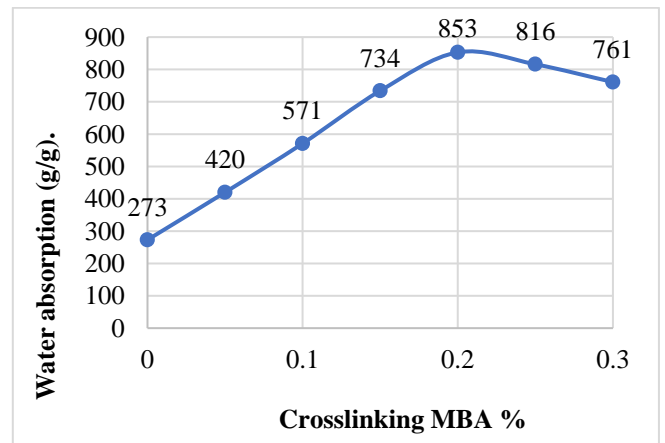


Fig. 8 Effect of crosslinking concentration on water absorbency

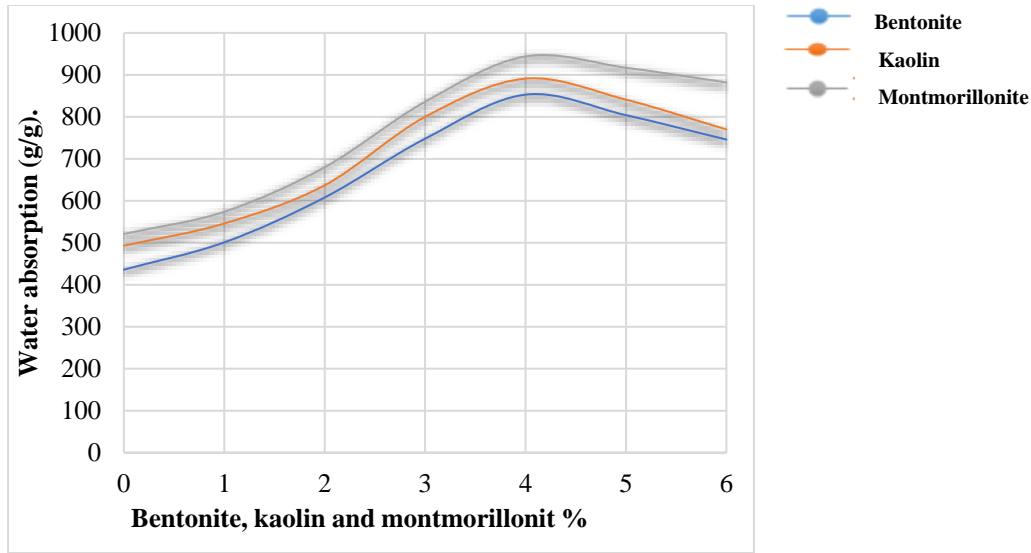


Fig. 9 Effect of minerals concentration on water absorbency

Table 1. Effect of starting material concentrations on the water absorption capacity

№	Starch:AM	Bentonite %	Kaolin %	Montmorillonite %	Water absorption (g/g)
1	1:1	5			638
	1:2				853
	1:3				815
2	1:1		4		662
	1:2				891
	1:3				871
3	1:1			4	695
	1:2				944
	1:3				887

Fig. 9 When the concentrations of montmorillonite and kaolin are higher than 4%, bentonite concentration is higher than 5% (relative to the mass of starch and acrylamide), the water absorption of hydrogels decreases. When their amount increases, the polymer strongly affects the binding points of the chain, and as a result of hindering the chain's growth, the polymer's molecular mass decreases.

As a result, the water absorption of the hydrogel decreases. As seen from Table 1, hydrogels exhibit the best water absorption properties when the molar ratio of starch and acrylamide is 1:2 in the synthesis of hydrogels.

4.4. The effect of Sodium Chloride Concentration On Hydrogel Water Absorption

As seen from Fig. 10, the water absorption capacity of St-g-PAM/Bentonite is inversely proportional to the concentration of the sodium chloride solution.

The osmotic pressure difference is a driving force in the water absorption phase of St-g-PAA/Bentonite. Therefore, hydrogels have a strong water absorption ability in a low-concentration NaCl solution.

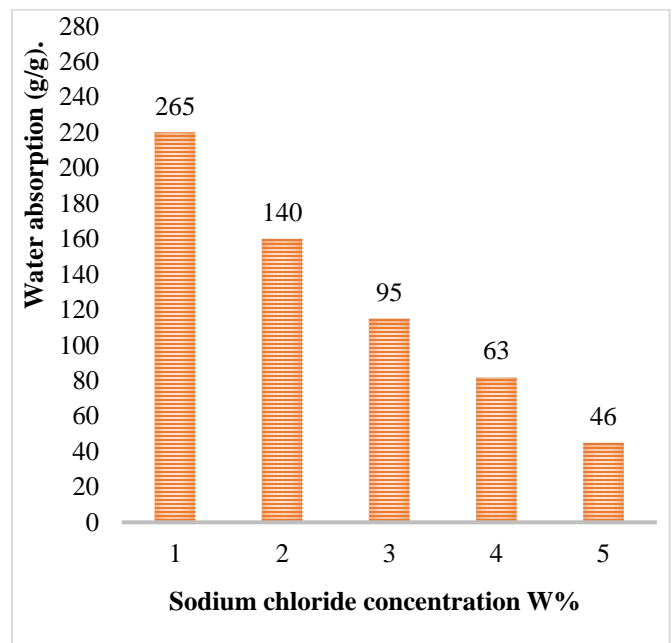


Fig. 10 The effect of sodium chloride concentration on hydrogel water absorption

5. Conclusion

Starch and bentonite, kaolin and montmorillonite minerals are highly important in obtaining semi-synthetic superabsorbent hydrogels. Starch, bentonite, kaolin, and montmorillonite are abundant, cheap, and harmless raw materials. These minerals increase the pores in hydrogels, resulting in improved water absorption and reducing the cost of superabsorbent hydrogels. These hydrogels play an important role in saving water and mineral resources in agriculture.

St-g-AM/B-based hydrogels store rainwater and deliver it to plants through the root system. St-g-AM/B-based hydrogels store rainwater and deliver it to plants through the root system; as a result, it prevents the plants from drying out due to lack of water.

Acknowledgments

Many thanks to Termez State University and Tashkent Scientific Research Institute of Chemical Technology, which closely support this research work.

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