

Original Article

Synthesis Hydrogels based on Starch-Graftacrylonitrile/Bentonite

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Abstract - This research aims to obtain low-cost, high-performance agricultural hydrogels with mineral retention based on natural polysaccharide copolymer. It is determined that the swelling properties of hydrogels depend on the concentration of the starting material, the reaction temperature and time of the acidic and alkaline medium, and the concentration of ions in the solution. The obtained hydrogels' water absorption and retention properties were determined in aggressive environments such as salty, acidic and alkaline. The swelling of hydrogels was tested in solutions of salts NaCl, CaCl₂ and AlCl₃ ions. When starch and bentonite are added to the hydrogel polymer chain and matrix, it was found that its water absorption increased by 25%, water retention time increased by 20%, and water consumption was reduced by 20-25%.

Keywords - Acrylonitrile, High swelling hydrogel, Initiator, Montmorillonite, Saponification, Sodium bicarbonate, Starch.

1. Introduction

Hydrogels are three-dimensional polymer networks capable of absorbing large amounts of water but remain insoluble due to chemical or physical crosslinks between individual polymer chains [1]. The polymer chain contains hydrophilic or functional groups dissociating in an aqueous medium, creating a crosslinked hydrogel structure. The polymer hydrogel is a unique sorbent, a hydroheterogeneous sorbing system. The dispersed phase is a spatial network formed by polymer macromolecules, and the water distributed in it is a dispersed medium [2-3]. They consist of long polymer chains, which are crosslinked with each other by transverse covalent bonds into a single spatial network. The general principles of the effect of absorbents on the soil's water regime and the plants' moisture supply are that when introduced into the soil and the root layer by uniform distribution, the absorbent granules are located in the pores.

When moisture enters, they swell, increasing moisture retention and favorable conditions for growth and plant development [4]. Chemically crosslinked hydrogels are synthesized using the following reactions: 1) radical polymerization, 2) polycondensation, 3) radiation polymerization [5, 6]. After the reaction, crosslinks between different polymer chains formed, and the networks thus obtained exhibited viscoelastic and sometimes purely elastic behavior. It also provides the necessary mechanical strength and physical integrity of hydrogels. There are two main

classes of Superabsorbent (SAP): synthetic (petrochemical-based) and natural (biopolymers) [7]. SAPs used for commercial purposes are produced from non-renewable petrochemical resources, especially monomers based on acrylic acid and acrylamide [8-10]. Several million tons of SAP synthetic materials are produced yearly for various applications [11]. After their use in agriculture, synthetic hydrogels lead to environmental pollution because synthetic hydrogels do not decompose quickly. That is why a growing interest is in producing partially synthetic and partially natural SAP [12, 13].

The most important challenge in the field of biodegradable SAP is the synthesis or manufacture of fully biodegradable polymer-based superabsorbent materials that will rapidly and reversibly absorb water with good mechanical strength. Polymer hydrogels based on starch: Starch occupies a special position in the group of natural polymers. It is the main dietary source of carbohydrates. This polysaccharide accumulates in plants and is stored as granules in the chloroplasts of green leaves and amyloplasts of seeds, tubers, and legumes.

It is a homopolymer consisting of glucopyranose units linked to each other in two forms: a linear form, amylose, and a highly branched form, amylopectin. Starch-based hydrogels are produced to reduce the use of synthetic hydrogels in the environment [14]. The chemical modification of starch has



been studied in the synthesis of hydrogel. There are many types of chemical modification. The optimal method is the radical copolymerization of vinyl monomers and starch.

Researchers develop hydrogels based on potatoes, corn and soluble starches [15]. The formation of starch-based hydrogels involves the gelatinization of starch and its retrogradation to form a three-dimensional network. The first step is to break down the starch crystal structure to facilitate polymer chain interaction. Acrylic acid or acrylamide is often used to copolymerize starch [16, 17].

In this method, starch grafting is carried out using a solution with available reagents, such as acrylic acid, acrylamide, initiator, and binder [18]. Copolymerization of starch with acrylamide or acrylic acid makes it possible to obtain superabsorbents with high water absorption capacity.

Graft copolymerization is a widely used chemical method of obtaining hydrogels based on starch. Starch molecules and acrylamide or acrylic acid monomers are covalently grafted under the action of an initiator (potassium persulfate) and a crosslinking agent N, N'-methylene-bis-acrylamide [19]. Hydrogels are mainly obtained from synthetic materials, natural polysaccharides, and copolymerization of both classes. Recently, long-acting synthetic hydrogels have replaced hydrogels based on natural polysaccharides. These hydrogels are highly water-absorbing and non-toxic. Hydrogels can be synthesized from pure polysaccharides [20-21].

There are three main components in the synthesis of hydrogels: monomers, initiators, and binders. In addition, the time and temperature of the reaction's molar ratio of the monomers and the reaction medium are important. Literature analysis showed that most industrially available highly flexible hydrogels are made from synthetic polymers, mainly vinyl monomers containing acrylic or methacrylic acids. Nowadays, people seriously care about their health, so they quickly refuse products that pollute the environment and have a negative impact on health.

Therefore, the industry is increasingly using biodegradable and environmentally friendly products. Therefore, semi-synthetic superabsorbent hydrogels based on starch, bentonite and acrylonitrile were synthesized in this research work. These hydrogels can be used in agriculture to reduce water consumption, save mineral fertilizers and increase plant productivity [22].

2. Materials and Methods

2.1. Materials

The following reagents were needed for the synthesis of superabsorbent hydrogels: corn starch (St), acrylonitrile (AN) (purity 99%), potassium persulfate (KPS), potassium hydroxide (KOH), potassium hydroxide (NaHCO_3), and used bentonite brand "Navbakhor" (Uzbekistan).

2.2. Methods

The following technologies and methods were used to study the physico-chemical properties of the obtained product: Fourier Transform Infrared (FTIR) Analysis, Scanning Electron Microscope (SEM), water absorption analysis (Q), determination of water retention time of superabsorbent hydrogel and others.

3. Experimental Part

3.1. Preparation of Superabsorbent Hydrogel

The reaction was carried out in a laboratory reactor equipped with a mechanical stirrer, a refrigerator, a thermometer and nitrogen gas. In the reactor, 10 g of potato starch is mixed with 120 ml of distilled water. Then, the solution was stirred for 10 minutes under a nitrogen atmosphere to remove dissolved oxygen.

The solution was heated at 80 °C for 30 min to form a starch suspension. Then, the starch suspension was mixed with an initiator for 10 minutes. Acrylonitrile, binding reagent and bentonite powder were added to the mixture. The reaction was then carried out at 60 °C with stirring for 4 hours. A nitrogen atmosphere was maintained throughout the reaction. The obtained product was transferred to a 4% sodium hydroxide solution and hydrolyzed at 95 °C for 2 hours.

After hydrolysis, the obtained product was filtered and washed several times with distilled water. Unreacted starting monomers were removed. The washed product was dehydrated with methanol. The dehydrated sample was dried at 60 °C under vacuum to obtain a superabsorbent hydrogel.

4. Results and Discussion

4.1. Fourier Transmission Infrared Spectroscopy (FTIR) Analysis

Figure 1 shows the IR spectrum of the obtained superabsorbent hydrogel St-g-PAN/BC. The absorption line at 3383.14 cm^{-1} shows slight shifts associated with the presence of -OH groups in it. In the regions of 2924.09 and 2852.72 cm^{-1} , the stretching vibration of the CH_2 and CH_2 groups, respectively, is observed. The absorption region at 1716.65 cm^{-1} is the absorption region relating to the carboxyl (COOH) and its salts - (COONa). The regions 1336.17 and 1556.65-1635.64 cm^{-1} are the stretching vibration of the $-\text{COO}^-$, $-\text{CONH}_2$, CONH groups. Area 1053.13 cm^{-1} represents the Si-O-Si group, area 989.48-950.91 cm^{-1} represents the Al-O-Al group, and area 555.50 cm^{-1} indicates the presence of the Al-O-Si group.

These functional groups represent the composition of bentonite added during hydrogel synthesis. During hydrolysis, the -CN group in acrylonitrile is replaced by other hydrophilic functional groups (-COOH, $-\text{CONH}_2$, COO^- , COOK , CONH). Therefore, the absorption region of 2227.8 cm^{-1} , corresponding to the -CN group in acrylonitrile, is not observed in the resulting superabsorbent hydrogel.

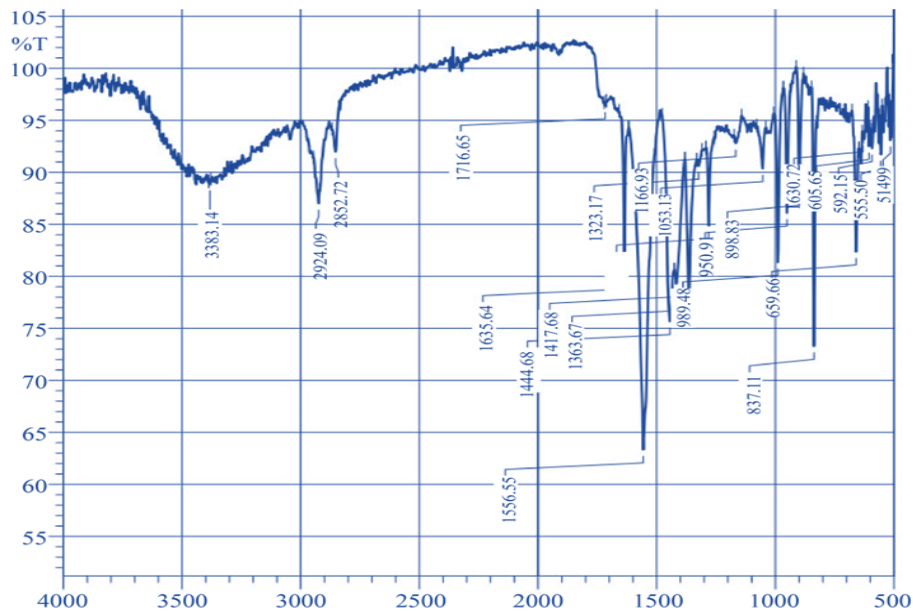


Fig. 1 FTIR spectrum of superabsorbent hydrogel

4.2. Morphology of Superabsorbent Polymer

The morphology of bentonite and the resulting hydrogel was studied using a scanning electron microscope (SEM) (Figure 2).

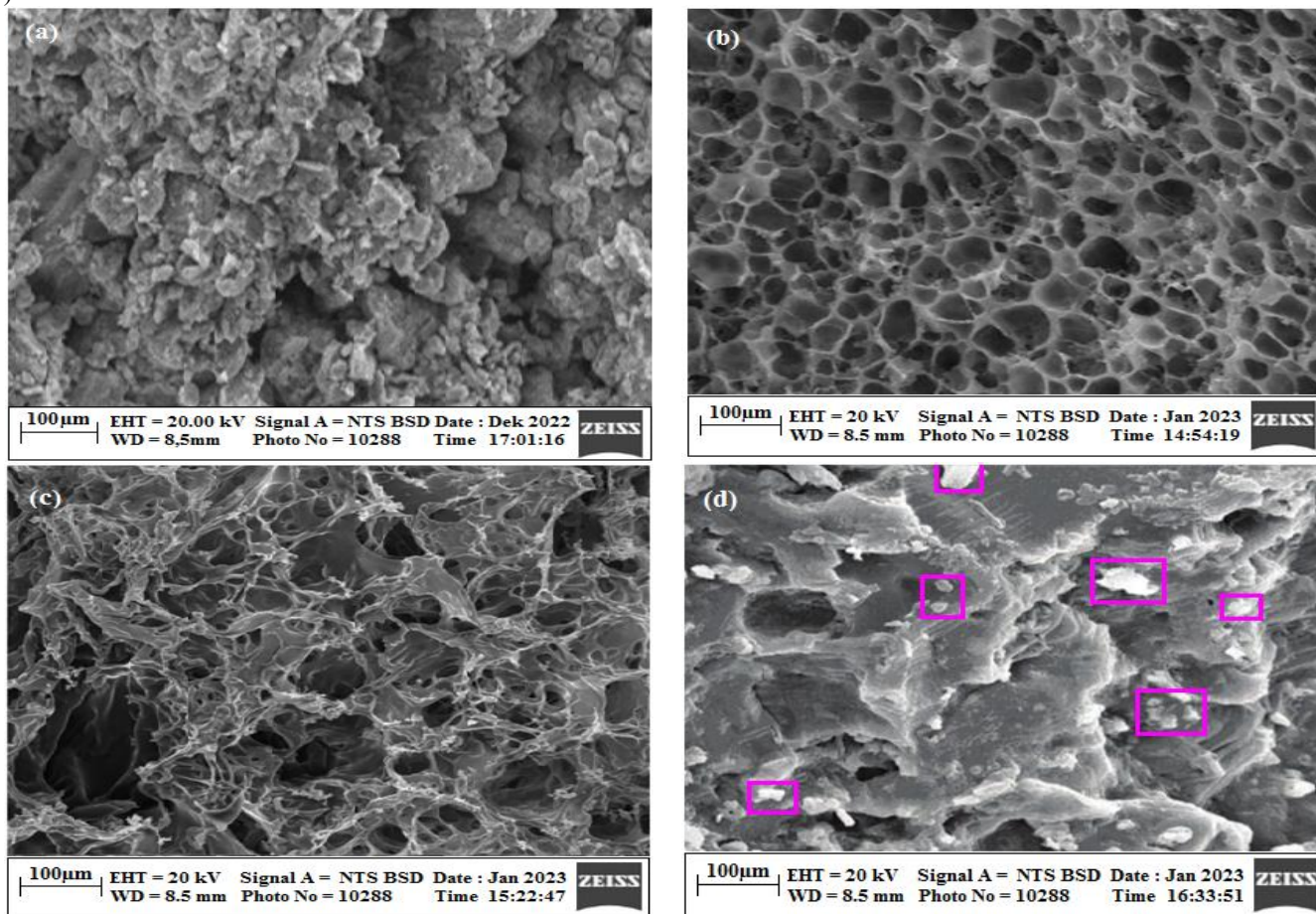


Fig. 2 (a) Bentonite, (b) Starch-g-PAN hydrogel, (c) Starch-g-PAN/Bentonite/NaHCO₃ hydrogel (d) hydrogel swollen in water (Starch-g-PAN/Bentonite/NaHCO₃)

During the synthesis of hydrogels, changes were observed after adding bentonite and sodium bicarbonate, so the morphology of the superabsorbent hydrogel was studied using SEM. Figure 2(a) bentonite Figure 2 (b) hydrogel obtained without bentonite and sodium bicarbonate, SEM image of a hydrogel based on superabsorbent hydrogel (Starch-g-PAN/Bentonite/NaHCO₃) preparation reactions by copolymerization of starch-acrylonitrile, bentonite and sodium bicarbonate. From the SEM image of the hydrogel in Figure 2 (b), it can be seen that the pores are small. Micro and macropores increase when adding bentonite and sodium bicarbonate during the synthesis of superabsorbent hydrogel (Figure 2 (c)).

It can be seen from Figure 2 that the hydrogel contains microparticles of bentonite, and this is seen from the SEM analysis of the hydrogel swollen in water (Figure 2(d)).

Bentonite increases the number of hydrophilic groups and creates micropores. Macropores are formed in hydrogels when carbon dioxide is released into the atmosphere, which is formed due to the decomposition of sodium bicarbonate.

The hydrophilic groups and large and small pores in hydrogels allow water to penetrate more quickly into the hydrogel, increasing its swelling capacity and reducing the swelling time.

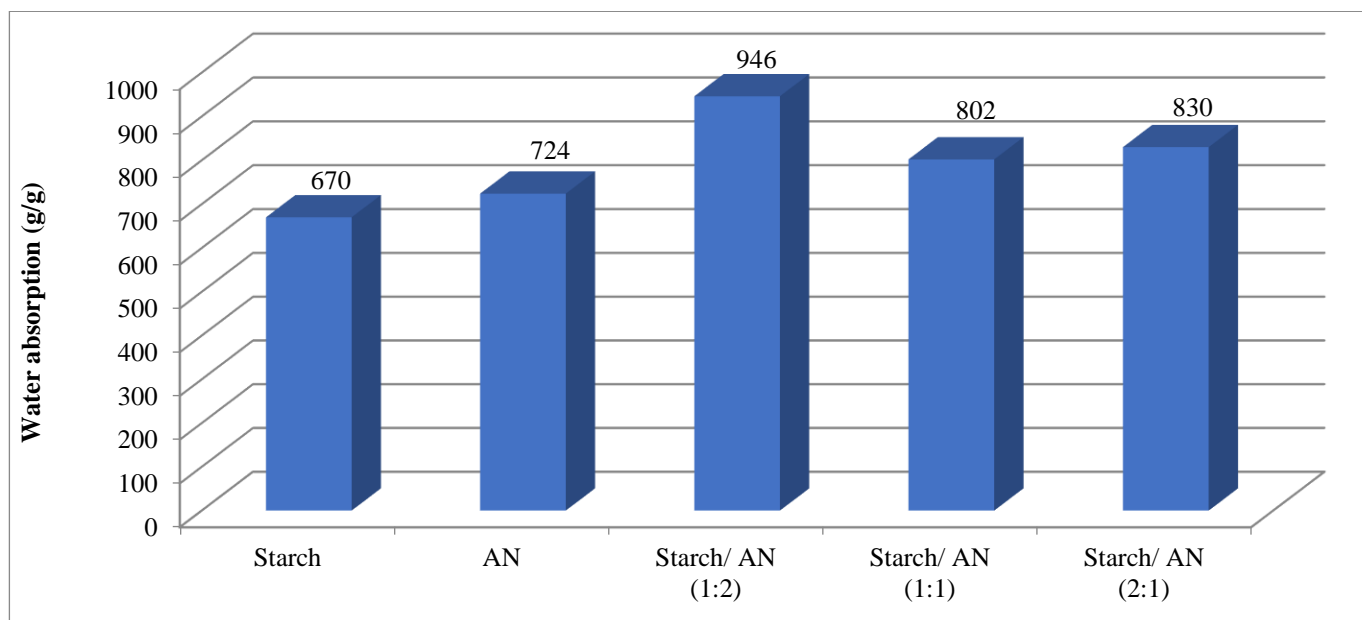


Fig. 3 Influence of mass ratios of starch and acrylonitrile on hydrogel swelling

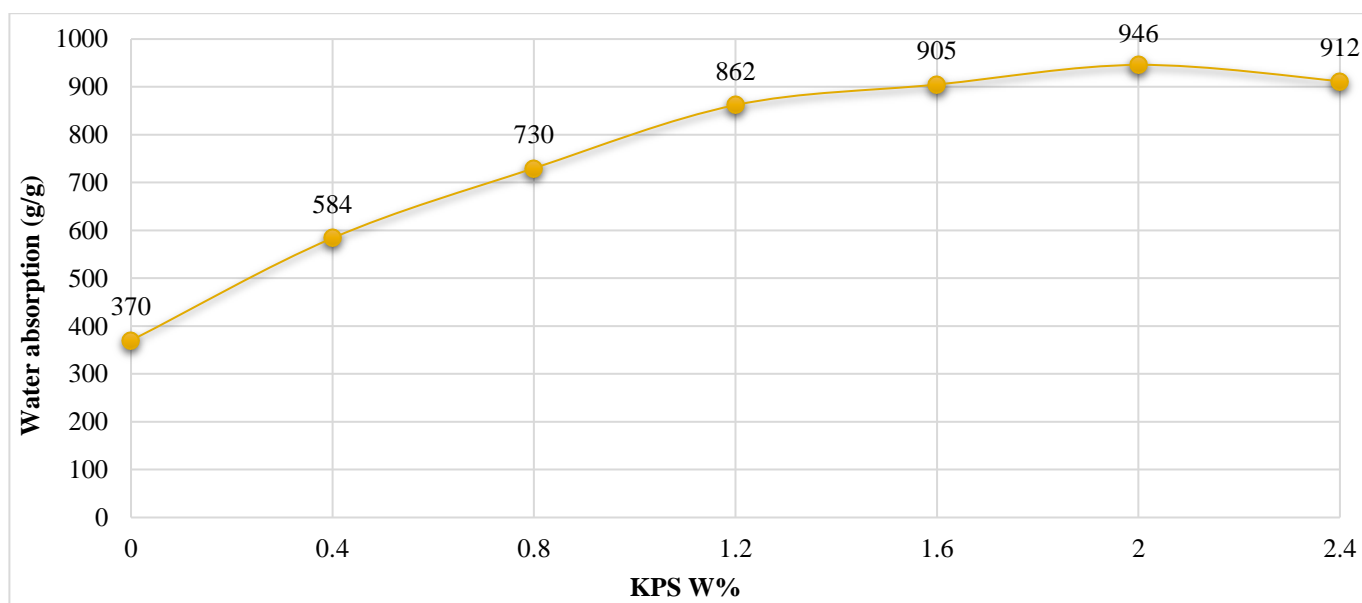


Fig. 4 Effect of initiator concentration on water absorbency

4.3. Influence of Mass Ratios of Starch and Acrylonitrile on Hydrogel Swelling

Due to the large amount of -OH in starch and the hydrophilic groups of carboxyl -COOH, sodium carboxylate -COONa, carbonyl -COO-, NH₂, NH formed as a result of the hydrolysis of acrylonitrile, and the hydrogel has a high swelling capacity. At a mass ratio of starch and acrylonitrile of 1:2, hydrogels exhibit high swelling. With a sharp increase in the mass of starch or vinyl monomer, the polymerization in the polymer chain is disordered, increasing the amount of substances not participating in the reaction. In this case, the hydrogels' molecular weight, reaction volume and swelling decrease (Figure 3). Figure 4 shows the effect of initiator concentration on water absorbency. The hydrogel has high water-absorbing properties at an initiator concentration (KPS) of 2% (relative to the mass of starch and acrylonitrile). If the number of initiators increases, and then many radical centers are created, which leads to uneven binding of monomers. Also, if the amount of initiator (KPS) is increased, the reaction may terminate prematurely.

4.4. Effect of Reaction Temperature on Water Absorbency

The reaction was carried out in the temperature range of 30 - 80 °C, and the effect of the reaction temperature on hydrogel swelling was studied. (Figure 5). From the data presented in Figure 5, it can be understood that the water

absorption of the hydrogel increased significantly when the reaction was carried out at 70°C. When the reaction is carried out at a low temperature, the degree of polymerization is low, and the water absorption capacity of the hydrogel is low due to the short chain formed. An increase in the reaction time leads to an increase in the degree of crosslinking of the polymers. This leads to a decrease in water absorption. Thus, a decrease or increase in temperature and reaction time leads to a decrease in the swelling of hydrogels.

4.5. Determination of Water Retention Time of Superabsorbent Hydrogel

1 g of hydrogel (M₁) was completely soaked in distilled water in a 1000 ml beaker. The excess water in the beaker was then removed using a Buchner funnel. As a result, only the water-soaked hydrogel remained in the beaker, while the hydrogel in the beaker was stored at 35 °C. Overall weight loss was observed every 2 days. The amount of water evaporated was determined using the following equation (1), and the average value was obtained from 3 experiments.

$$WRV = \frac{M_1}{M_2} * 100$$

Here, WRV water holding capacity (g/g) M₁ – the weight of the sample remaining after a specific time and M₂ – the mass of the sample completely immersed in water.

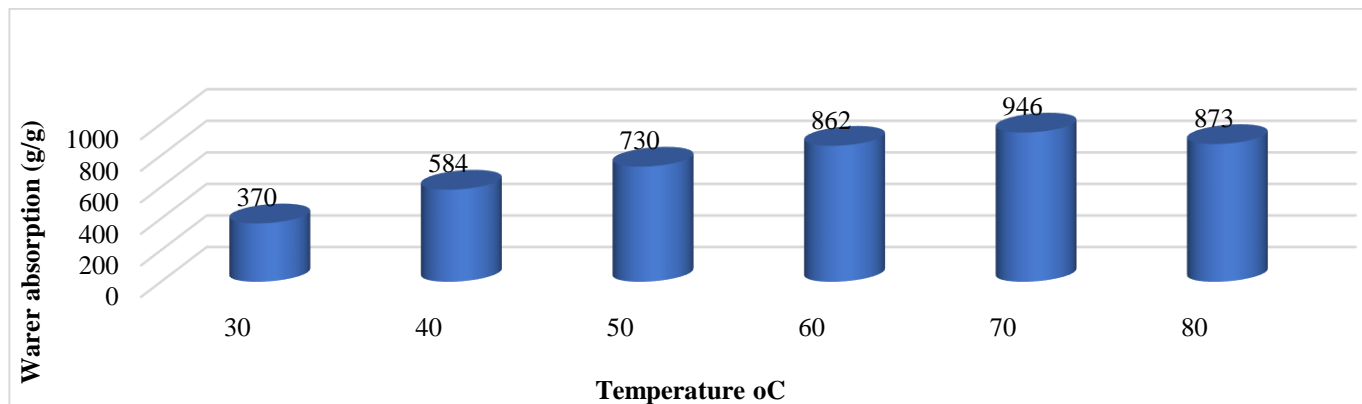


Fig. 5 Effect of reaction temperature on water absorbency

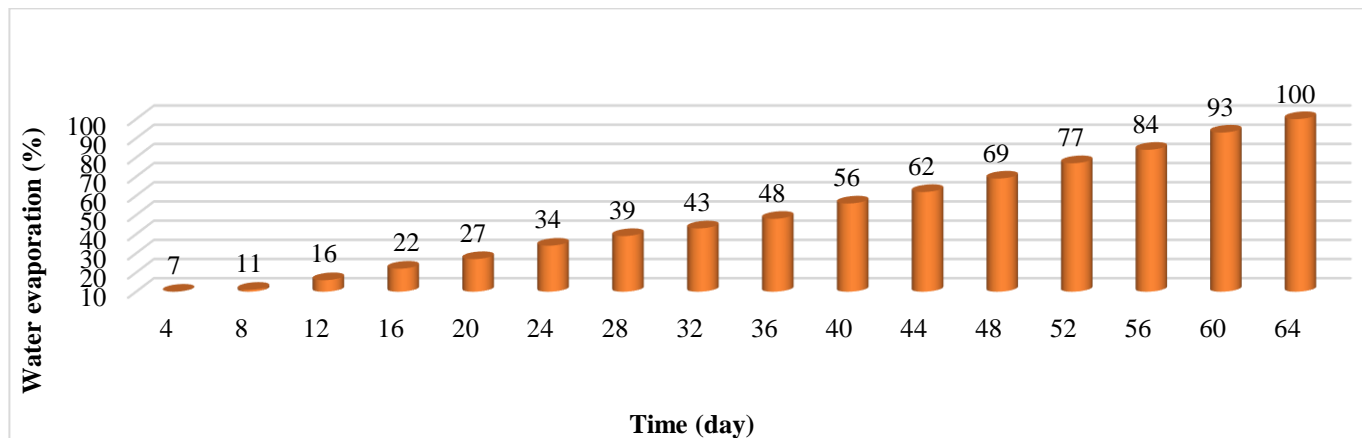


Fig. 6 Determination of water retention time of hydrogel

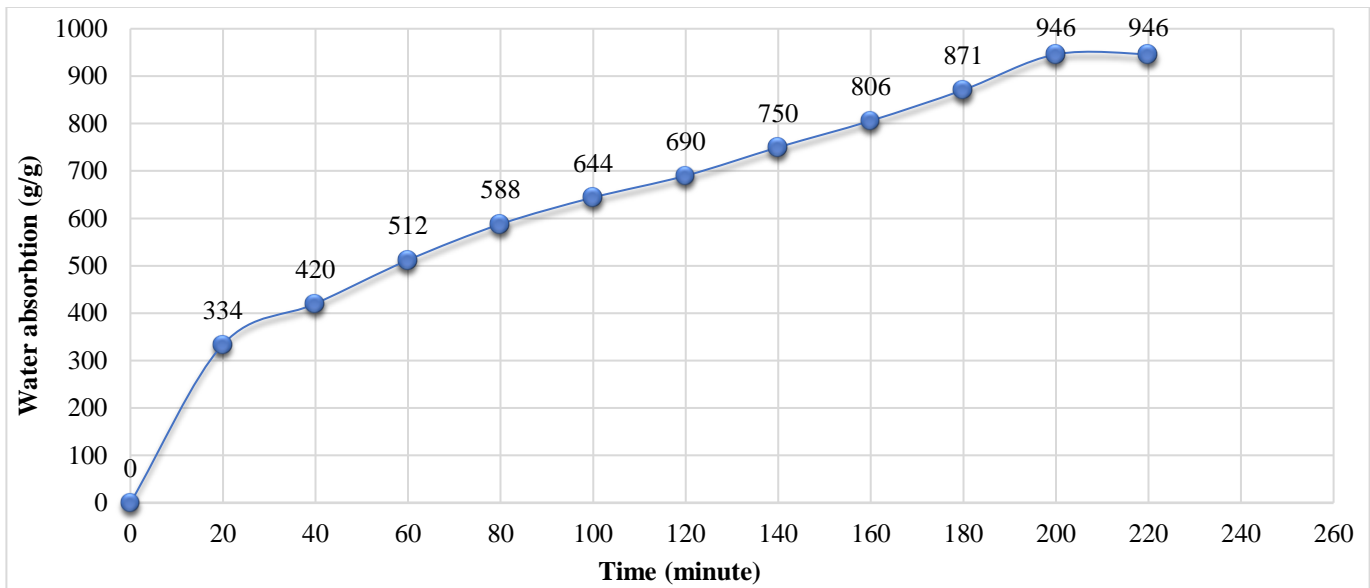


Fig. 7 Determination of the swelling time of the hydrogel in distilled water

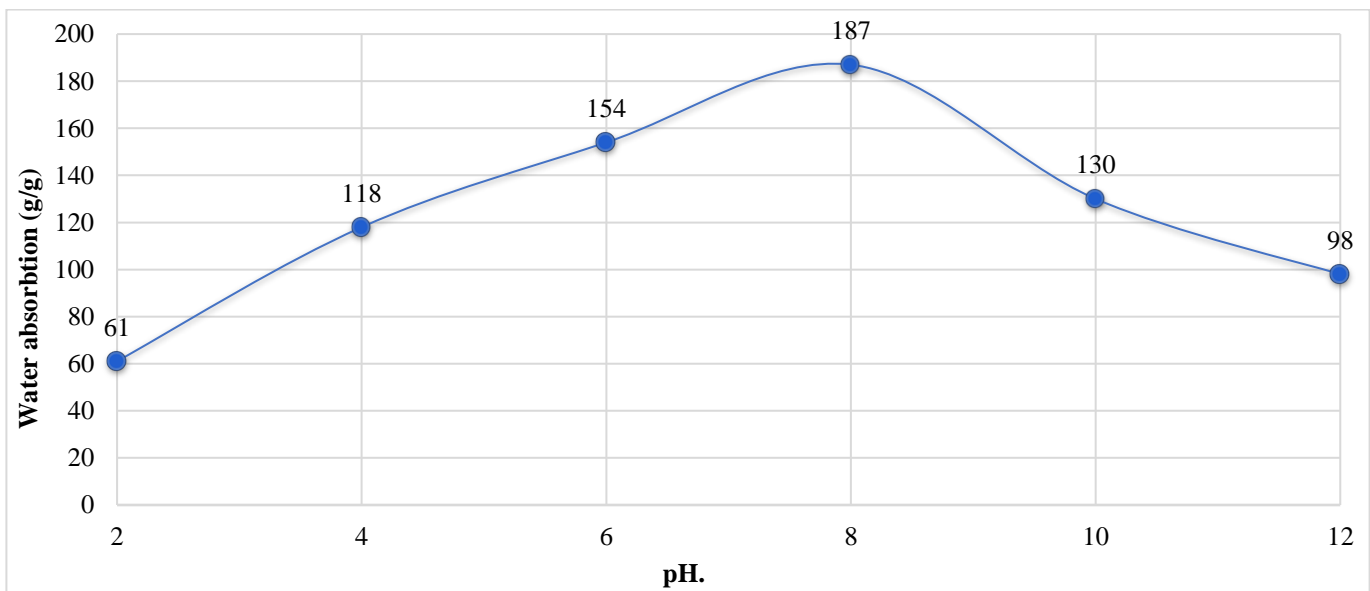


Fig. 8 Swelling of hydrogel in different pH environments

The acid decomposition of bentonite and sodium bicarbonate was used to obtain macro- and microporous hydrogels. As a result of sodium bicarbonate decomposition, carbon dioxide is formed, and this gas creates macropores when released into the atmosphere. Although all synthesized hydrogels had pores, they differed in thickness. The swelling of the resulting hydrogels depends on their composition, preparation method, and pore size. The reaction product becomes dense, brittle, and hard during the polymerization of highly concentrated monomer solutions without adding foaming agents. Therefore, foaming agents are added to preserve the pores, and for dehydration, such products are washed with ethyl alcohol. Dehydration of the obtained product with ethanol prevents the narrowing of its pores.

Ethanol can be removed from the product by short drying. This process also removes unreacted residual products. Also, the swelling of hydrogels depends on the size of the mineral particles and the surface pores.

4.6. Effect of Different pH Environments on Hydrogel Swelling

The swelling of the obtained hydrogel was studied at various pH values 2-12 (Figure 8). It can be seen that the swelling of hydrogels increases from pH=2 to 8. When the pH is above 8, the swelling of the hydrogel is reduced. Functional groups $-\text{COO}^-$ and $-\text{COOH}$ in anionic polymers can be converted into each other. In an acidic environment, carbonyl groups COO^- are converted to carboxyl groups $-\text{COOH}$.

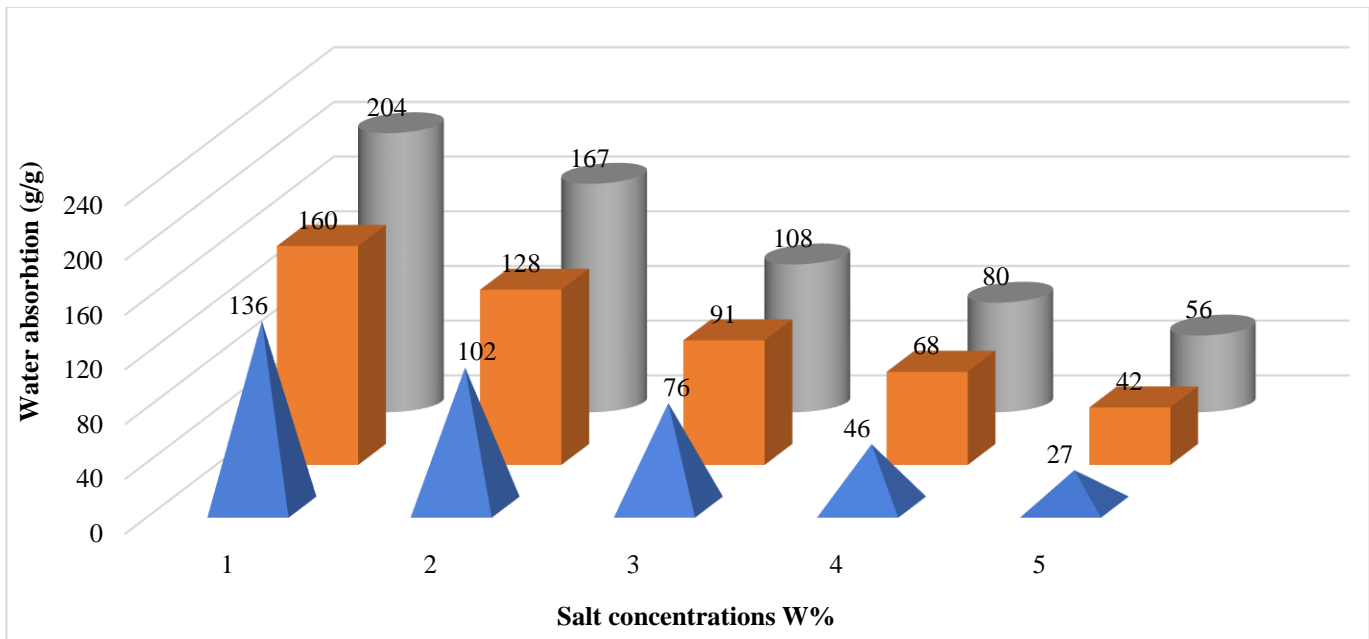


Fig. 9 For hydrogel swelling, sodium chloride (NaCl), calcium chloride (CaCl₂), aluminum chloride (AlCl₃) effect of concentrations

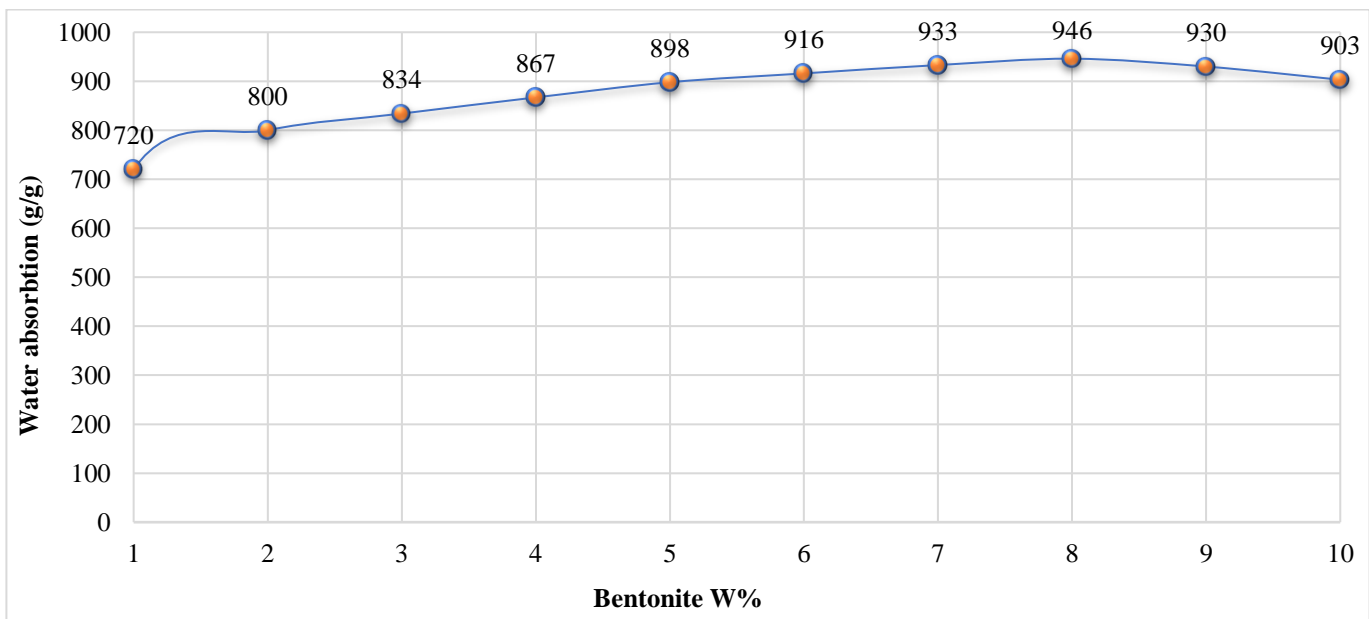


Fig. 10 Effect of bentonite concentration on hydrogel swelling

4.7. Determination of Water Absorption of Hydrogel in Different Salt Solutions

The increase in salt concentration is inversely proportional to the swelling of hydrogels. This phenomenon is associated with an increase in the number of ions and a decrease in the osmotic pressure drop due to an increase in the concentration of salts in the solution. Therefore, hydrogels have a high water-absorbing capacity in low-concentration salt solutions. The effect of solutions of various salts, including monovalent (NaCl), divalent (CaCl₂), and trivalent (AlCl₃) ions, on the swelling of hydrogels was studied. The

swelling ability of hydrogels in different concentrations of salt solutions was tested at a temperature of 35 °C. It can be seen that the solubility depends on the type of salt, its concentration, and the valence see in Figure 9.

4.8. Effect of Bentonite Concentration on Hydrogel Swelling

When the concentration of bentonite is above 8%, it greatly affects the binding points of the polymer chain and inhibits chain growth (Figure 10). As a result, the molecular weight of the polymer, and the water absorption of the hydrogel is reduced. Bentonite contains additional oxides

such as TiO₂, Fe₂O₃, MgO, CaO, Na₂O, K₂O, P₂O₅, SO₃, FeO. These additional oxides interfere with the polymerization process.

5. Conclusion

Starch and bentonite minerals are of great practical importance in obtaining semi-synthetic superabsorbent hydrogels. Starch and bentonite 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 are vital in saving water and mineral resources in agriculture. Starch-g-PAN/Bentonite/NaHCO₃ 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.

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