



# SYNTHESIS OF SUPERABSORBENT HYDROGELS BASED ON STARCH- CHITOSAN HYBRID

Turaev Khayit<sup>[a]</sup>, Kholnazarov Bakhodir<sup>[b]\*</sup>, Djalilov Abdulakhad<sup>[c]</sup>

Article History: Received: 10.09.2022

Revised: 15.10.2022

Accepted: 16.11.2022

**Abstract:** The aim of this study is to obtain a biodegradable, inexpensive and highly water- swellable agricultural hydrogel by radical copolymerization of a starch-chitosan (St-g-CTS) hybrid with acrylic acid (AA). When examining the synthesized ((St/CTS)/PAA) based hydrogel using a scanning electron microscope (SEM), it was found that it has pores necessary for absorption and desorption. IR spectroscopy and differential thermogravimetric analyzes of the obtained hydrogels are investigated. The water absorption of the resulting hydrogels in distilled water and saline solutions of various concentrations was determined. Swelling in distilled water was 550 g/g, in saline solutions 60 to 127 g/g (0.9% saline solution). The dependence of the degree of swelling of the synthesized superabsorbent hydrogels on the molar ratio of starch, chitosan and acrylic acid, the amount of initiator and binder, the duration and temperature of the reaction has been determined. The use of synthesized hydrogel in agriculture helps to reduce the consumption of irrigation water, reduces the drying of plants, ensures the retention of fertilizers in the soil around the roots, and increases the growth rate and productivity of plants.

**Keywords:** Starch-chitosan, vinyl monomer, copolymerization, water absorption, acrylic acid grafting.

[a]. Department of Analytical and Inorganic Chemistry, Faculty of Chemistry, Termez State University

[b]. Tashkent Scientific Research Institute of Chemical Technology

[c]. Department of Analytical and Inorganic Chemistry, Faculty of Chemistry, Termez State University

\*Corresponding Author

E-mail: baxodir.xolnazarov@rambler.ru

DOI: 10.31838/ecb/2022.11.11.018

## INTRODUCTION

An important feature of superabsorbent hydrogels is that they absorb water at a high level in a short time and return it when needed (1,2). This expands the possibilities of their use in various fields - medicine, food industry, agriculture and other areas. (3,4). One of the most important methods for synthesizing superabsorbent hydrogels by copolymerizing vinyl monomers with natural polysaccharides such as starch (5), chitosan (6,7,8,9), and cellulose (10) is radical polymerization (11). This method makes it possible to obtain a non-toxic, antibacterial, biodegradable and inexpensive product. Chitosan contains free amino acids and hydroxyl groups, which allow it for cross-linking and chelation reactions. Interest in chitosan is due to its unique chemical nature (partially deacetylated form of chitin), which has several advantages. The use of chitosan for acrylic acid grafting made it possible to obtain materials with high swelling properties. However, the low mechanical properties of such materials limit their sectors of application (12). To overcome these shortcomings, chitosan should be

grafted with cellulose, hydroxypropyl cellulose and other natural polymer materials. Cellulose is a natural polymer material and is the most abundant biopolymer found mainly in wood, cotton and other sources (13). The performance of agricultural hydrogels depends on temperature, relative humidity, soil type and various other factors. The advantage of hydrogels based on the cellulose-chitosan hybrid is that they are environmentally friendly, retain a large amount of water, are inexpensive, and are biodegradable. Starch-chitosan-based hydrogels can be reused several times due to good adsorption and desorption properties (14). Rapid population growth and per capita spending will further increase the demand for fresh water in the world, which may cause irreparable events in a few years. Therefore, in this research work, a new agricultural hydrogel was synthesized, which absorbs a large amount of water and returns it to plants through the root system when necessary. Starch- chitosan hybrid (St/CTS) and acrylic acid were used in the synthesis of superabsorbent hydrogel ((St/CTS)/PAA). Hydrogel based on ((St/STS)/PAA) increases the efficiency of water use and prevents plants from drying out under stress. Also, this hydrogel increases the porosity of the soil and reduces its pressure. Also, the ((St/STS)/PAA)-based hydrogel reduces water evaporation, allows it to penetrate deeper, and prevents leaching of nutrients.

## MATERIALS AND METHODS

### Materials

Potato starch (St), chitosan (CTS) (purity 85%), acrylic acid (AA) and ammonium persulfate (APS), N,N'-methylenebisacrylamide (MBA). Also, chemicals such as thiourea, formaldehyde and acetic acid were purchased from the local market.

**Fourier Transform Infrared (FTIR) Analysis**

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

**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.

**Differential Scanning Calorimetry (DSC) Analysis**

The thermal stability of the sample was analyzed by differential scanning calorimetry (DTG-60, SIMULTANEOUS DTA-TG APPARATUS SHIMADZU, Japan). For DSC analysis, the sample (2-3mg) was coated with a gold coating. The test was carried out in the temperature range of 25- 600  $^{\circ}\text{C}$ , at a heating rate of 10  $^{\circ}\text{C min}^{-1}$ .

**Water absorption analysis (Q)**

1g of the hydrogel dried in a vacuum drying cabinet at 60  $^{\circ}\text{C}$  to a constant mass was taken and immersed in 1L of distilled water and various salt solutions for 24 hours. Then, the pores of the water-soaked hydrogel (M2) 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 dry sample, M1 is the weight of the dry sample, and M2 (g) is the weight of the swollen sample (15).

**Determination of water retention time of superabsorbent hydrogel.**

The water-retention property of hydrogel was determined at 35  $^{\circ}\text{C}$  temperature. The hydrogel was first immersed in deionized water and brine, respectively, till the swelling equilibrium was reached. Next, the samples were taken out and placed in a drying box at 35  $^{\circ}\text{C}$  to be ventilated and dried.

$$WRV = \frac{M_2}{M_3} \times 100 \quad (2)$$

Where: WRV water retention value M2 is the weight of the sample remaining after a certain time and M3 is the weight of the sample completely immersed in water (16).

**Preparation of cross-linked starch-chitosan (St/CTS) hybrid.**

8.05 g of chitosan was dissolved in 200 ml of a 3% aqueous solution of acetic acid. Also, 8.1 g of potato starch was mixed

in 100 ml of water at 80  $^{\circ}\text{C}$  for 25 minutes using a mechanical mixer to form gelatin. Then, the chitosan solution was filtered. Filtered chitosan and starch gelatin were mixed in 250 mL of distilled water at room temperature for 12 h. The resulting solution was poured into a petter cup and dried at 35  $^{\circ}\text{C}$  for 4 days. During this period, chitosan completely adheres to starch. Thiourea-formaldehyde resin was used as a binder to cross-link the starch- chitosan (St/CTS) hybrid. To prepare thiourea-formaldehyde resin, 1.52 g of thiourea was dissolved in 25 ml of distilled water and 1.62 ml of 37% formaldehyde solution was added to it, and the solution medium was adjusted to pH-4 using acetic acid and the reaction was carried out at 90  $^{\circ}\text{C}$  for 6 conducted for hours. A colorless viscous product, thiourea-formaldehyde resin, was formed. So'ngra unga kraxmal va xitozandan iborat 16 g aralashma aralashtirildi. After that, the reaction to obtain the starch-chitosan (St/CTS) hybrid was carried out at 90  $^{\circ}\text{C}$  for 4 hours. The reaction was carried out in an aqueous solution medium. The obtained product was dried at a temperature of 45  $^{\circ}\text{C}$  for two days and it was crushed to a size of 0.1 mm. A cross-linked starch- chitosan (St-g-CTS) hybrid was formed.

**Preparation of superabsorbent hydrogel based on cross-linked starch-chitosan (St-g-CTS) hybrid.**

6.46 g of the cross-linked starch-chitosan (St-g-CTS) hybrid was weighed and added to 100ml of distilled water in a 250 ml three-necked flask equipped with a mechanical stirrer, nitrogen gas and a reflux condenser. The oxygen present in the solution was removed from the solution for 15 minutes under nitrogen gas atmosphere. Then, 0.13 g of APS was added to form radicals on the surface of (St-g-CTS) hybrid. (The initiator first attacks the hydroxyl group on the outside of the polymer chain and forms free radicals, which are active sites and lead to the formation of a long polymer chain). After 20 minutes, 5.76 mL of 70% neutralized acrylic acid was added to the flask, along with 0.06 g of N,N'-methylenebisacrylamide as a binder. The polymerization reaction was carried out at 70  $^{\circ}\text{C}$  for 6 hours with stirring. Then, to remove unreacted residues, the sample was washed with 50% ethyl alcohol, then dried in a drying oven at 60 $^{\circ}\text{C}$ .

**RESULTS AND DISCUSSION****Fourier Transmission Infrared spectroscopy (FTIR) analysis.**

The double bond and COOH groups of acrylic acid interact with NH2 and OH groups of chitosan and OH groups of starch to form a polymer chain. Figure 1 shows (a) the spectrum of starch, (b) the spectrum of chitosan, (c) the spectrum of the cross-linked (St-g-CTS) hybrid, and (d) the IR spectra of ((St/CTS)PAA).

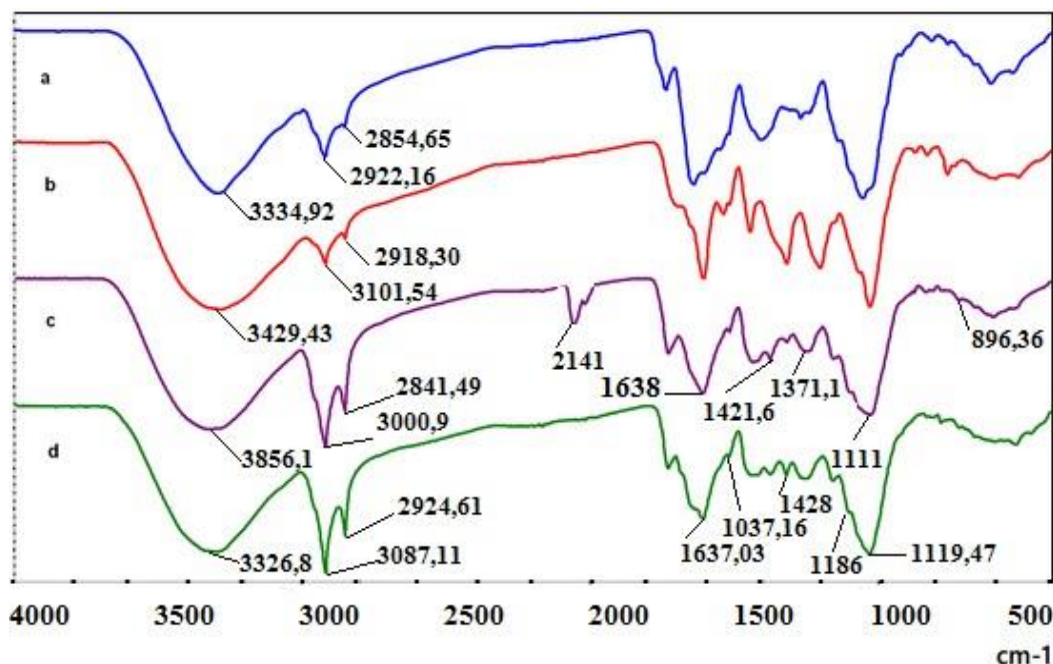


Fig. 1. FTIR of a) starch, b) (CTS), c) St-g-CTS-, d) ((St/CTS)-g-PAA)

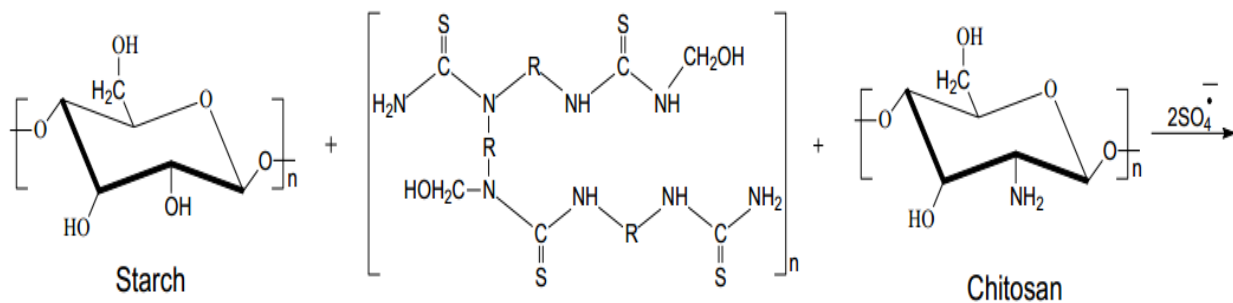
Figure 1 (c) it can be seen that the 3334.92 cm<sup>-1</sup> absorption region belonging to the OH group of starch extends to 1638 and 1111 cm<sup>-1</sup> absorption regions in its obtained hybrid (St-g-CTS).

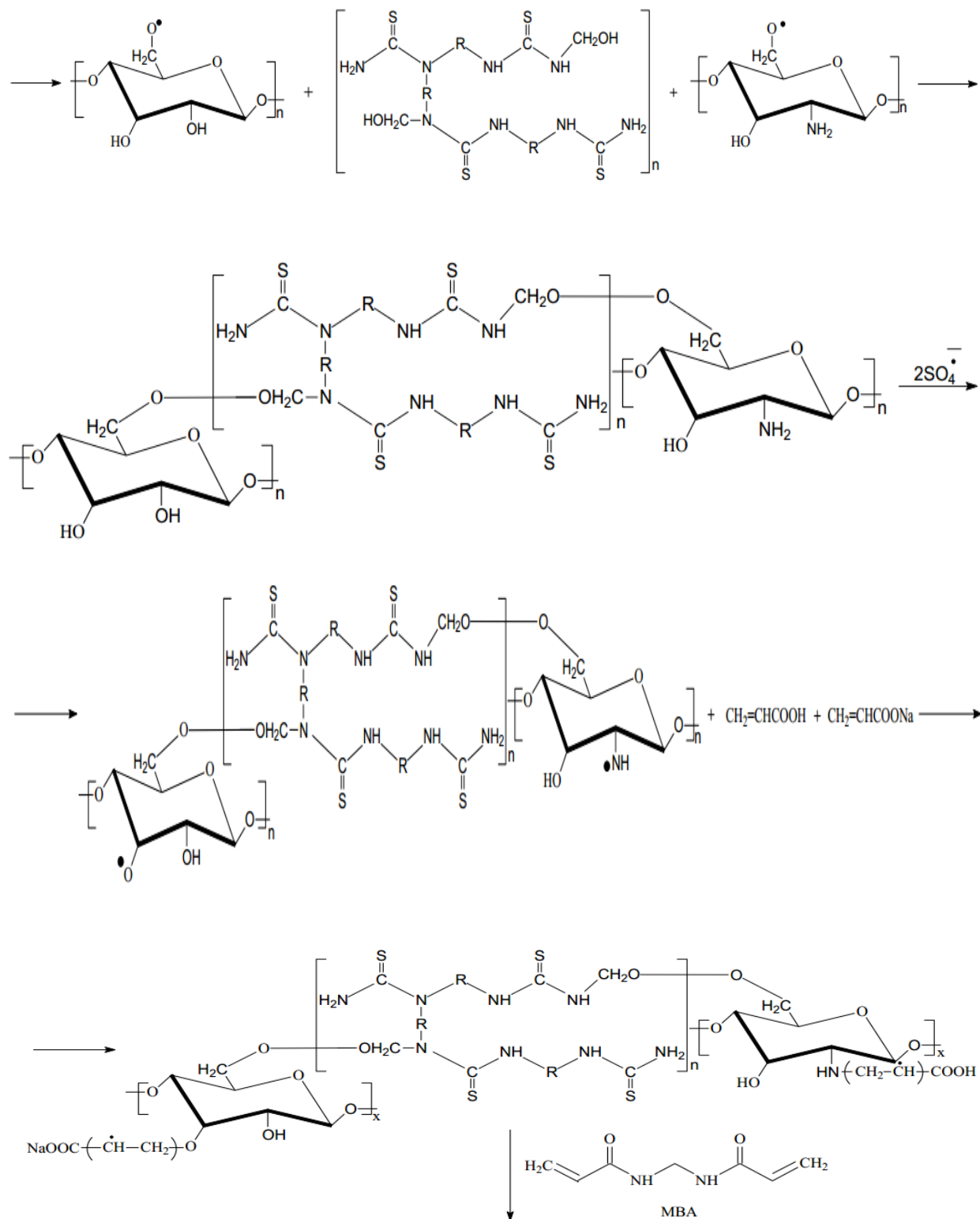
Areas that reveal the stretching of the 2922.16-2918.30 cm<sup>-1</sup> areas belonging to the CH<sub>2</sub> and CH groups of starch and chitosan appear, which can be seen in the 1371,1 and 896.36 cm<sup>-1</sup> areas. The spectra of 3429.43-3101.54 cm<sup>-1</sup> belonging to OH and NH groups of chitosan are represented by bands extending to 1421.6 cm<sup>-1</sup> area. The spectral change is mainly caused by the reaction between hydroxyl groups and urea methylol. The absorption areas of 3000.9 and 3856 cm<sup>-1</sup> in

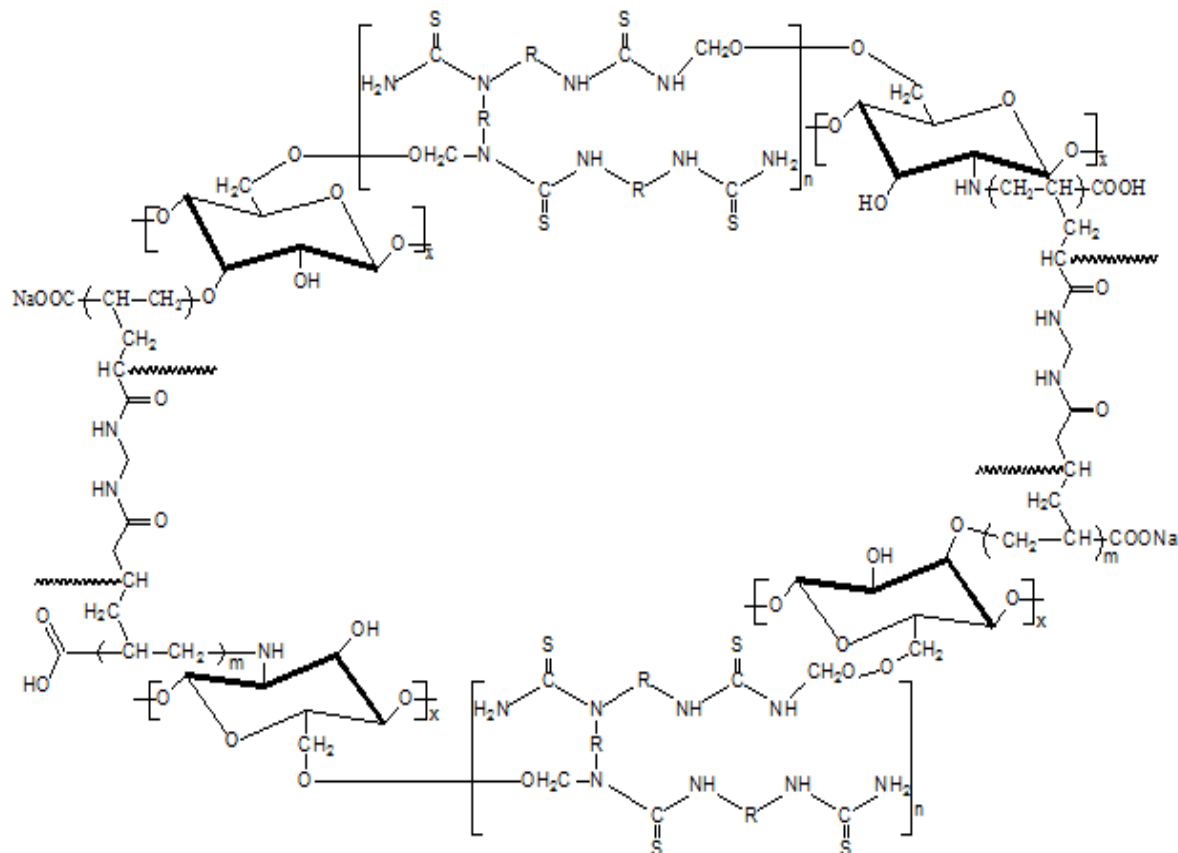
cross-linked (St-g-CTS) (c) hybrid are attributed to unreacted OH and NH functional groups. ((St/CTS)PAA)

(d) absorption areas at 1637.03, 1037.16 and 1119.47 cm<sup>-1</sup> are due to the stretching of the OH group. One can see lines belonging to C-O-C in the region of 1186 cm<sup>-1</sup>.

First, radical centers were formed in the initiator effect for grafting starch and chitosan using a binder. The cross-linked first network is a starch-chitosan hybrid, while methylenebisacrylamide MBA (cross-linker) cross-linked with grafted PAA chains forms the second network. It can be seen that the COOH group of acrylic acid is bonded to each other and to the NH<sub>2</sub> groups in chitosan and the OH groups in starch. (Fig. 2).







**Fig. 2. A simplified scheme for starch–chitosan combination via chemical crosslinking using thiourea formaldehyde and reactions to obtain a superabsorbent hydrogel by copolymerizing their hybrid with acrylic acid in the presence of MBA.**

**Water absorption of the superabsorbent polymers**

Figure 3 shows the swelling potential of superabsorbent composites in distilled water. It can be seen that the distilled water absorption capacity of the hydrogel is 550 g/g. This indicates that there are enough hydrophilic groups such as

COO-, -COOH, -NH, NH<sub>2</sub> and OH in the polymer chain of the hydrogel. It can be seen that the number of such hydrophilic groups increased especially when starch and chitosan were grafted.

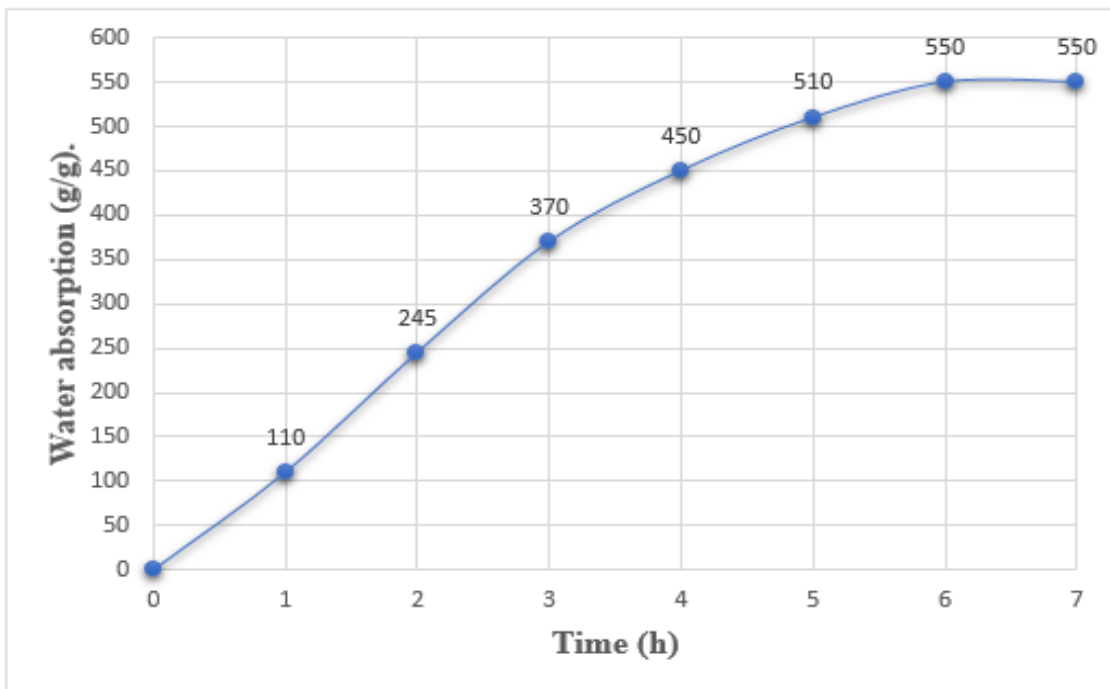


Fig. 3. Water absorption of the superabsorbent polymers.

**Determination of water absorption of hydrogel in different salt solutions**

Hydrogel water absorption in different salt solutions (NaCl, KCl, NH<sub>4</sub>Cl, MgCl<sub>2</sub>, CaCl<sub>2</sub>) was tested under the same conditions. (Fig. 4).

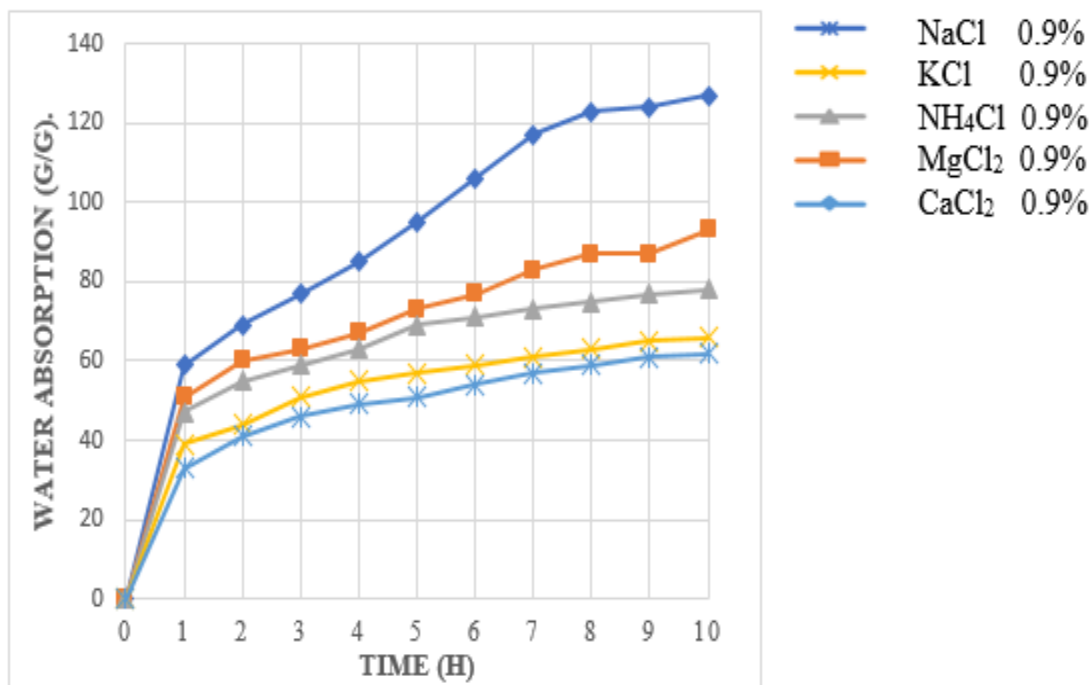


Fig. 4. Determination of water absorption of hydrogel in different salt solutions.

### Water retention analysis

The water retention time of 1g of hydrogel soaked in distilled water was studied at 35°C. The amount of water evaporation was monitored every 3 days. In figure 5, we can see that the

water stored in the hydrogel slowly evaporated completely over 36 days. Due to the fact that this hydrogel retains water for a long time, it prevents excessive watering in agriculture and drying of plants due to lack of water.

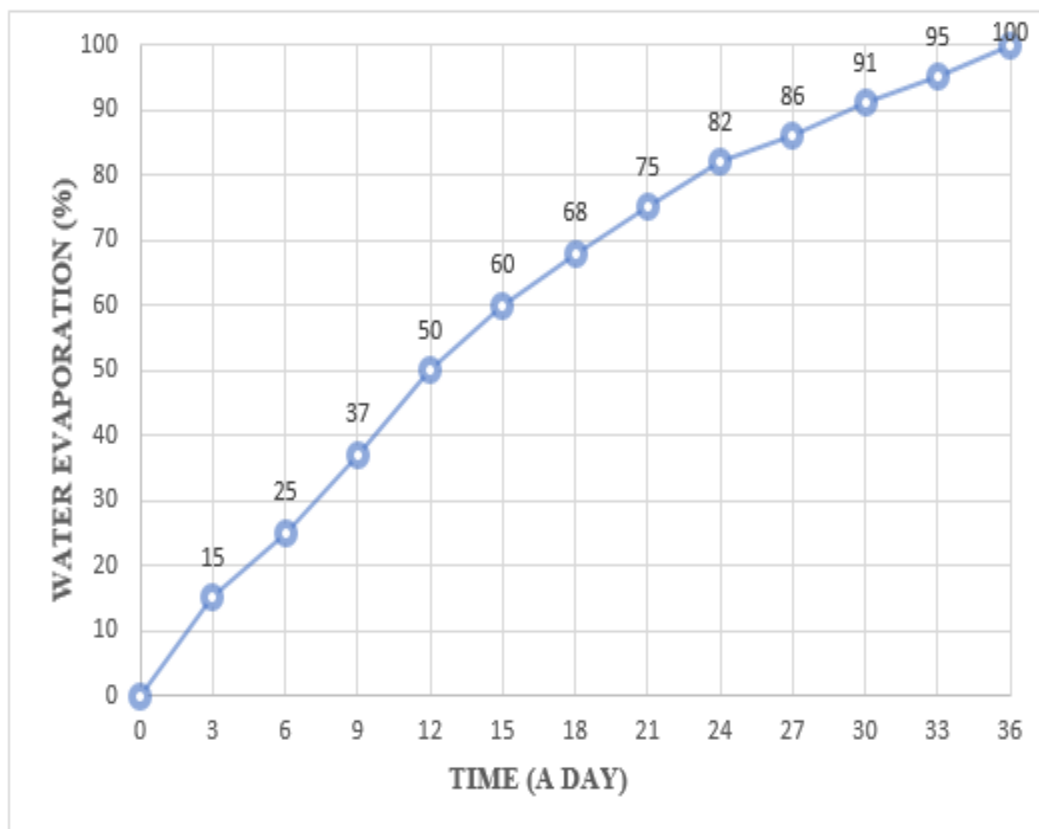


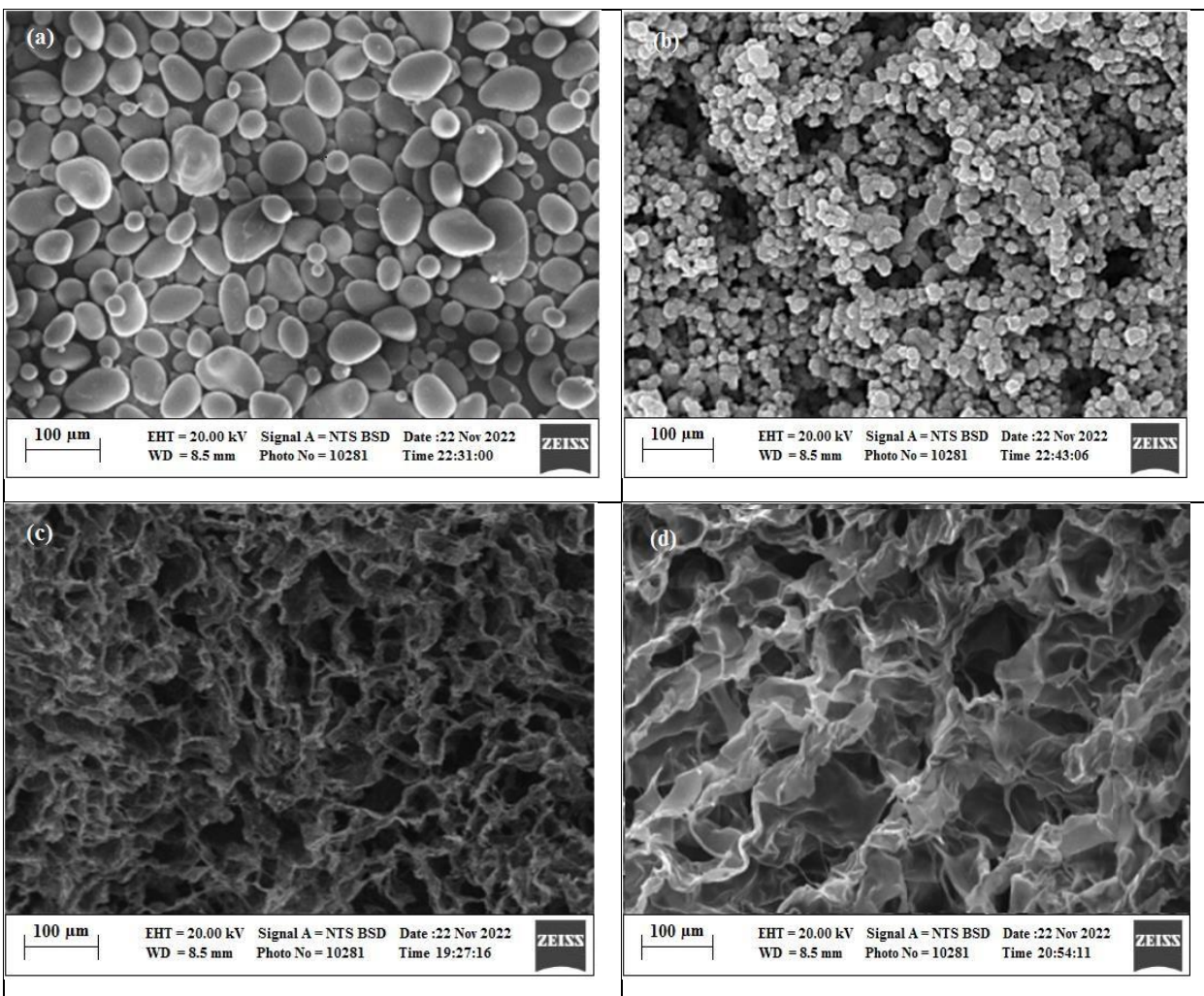
Fig. 5. Determination of water retention time of (St/CTS)/PAA hydrogel

### Morphology of superabsorbent polymer

Figure 6 morphological analysis of starch (a), chitosan (b), starch/chitosan ((St-g-CTS) (c) and starch/chitosan/poliacrylic acid (St/CTS)-g-PAA) hydrogel was studied using a scanning electron microscope. Joints and pores can be seen in the hydrogel based on (St-g-CTS) (c) hybrid and (St/CTS)-g-PAA (d). This means that a hybrid was formed on the basis of starch and chitosan and that the hybrid reacted with acrylic acid. These pores serve to absorb and release water. Also, through the pores,

the fertilizers contained in the hydrogels easily pass to the plant stem. When the hybrid (St-g-CTS) reacts with acrylic acid (AA), it can be seen that the pores are larger and there is a change in the color of the product.

In the synthesis of superabsorbent hydrogel, the O-Si-O and -OH groups in the added bentonite participate in the reaction. therefore, bentonite can increase the hydrophilic groups in the superabsorbent hydrogel (13).



**Fig.6. SEM micrograph of starch (a), chitosan (b), (St-g-CTS) (c), and ((St/CTS)-g-PAA) (d) based synthesized hydrogel**

#### Thermal stability of superabsorbent composites

To investigate the thermal stability of the synthesized ((St/CTS)-g-PAA)-based hydrogel, it was analyzed by differential-thermal and thermogravimetric methods (Fig. 7). In this case, the increase in temperature from 27.81 to 231.20 oC is due to a very small amount of water evaporation, where the mass loss is 1.435 mg or 15.184%. It can be seen that superabsorbent has the ability to retain water even at high

temperatures. At temperatures from 231.20 to 512.79 oC, it indicates the decomposition of carboxyl groups in the chain, where the mass loss is 3.819 mg or 40.408%. The next mass loss refers to the breaking of bonds in the polymer chain at temperatures between 512.79 and 601.07 oC, where the mass loss is 0.108 mg or 1.143%. In general, as a result of the differential- thermal method, it was found that ((St/CTS)-g-PAA)-based hydrogel is resistant to heat.



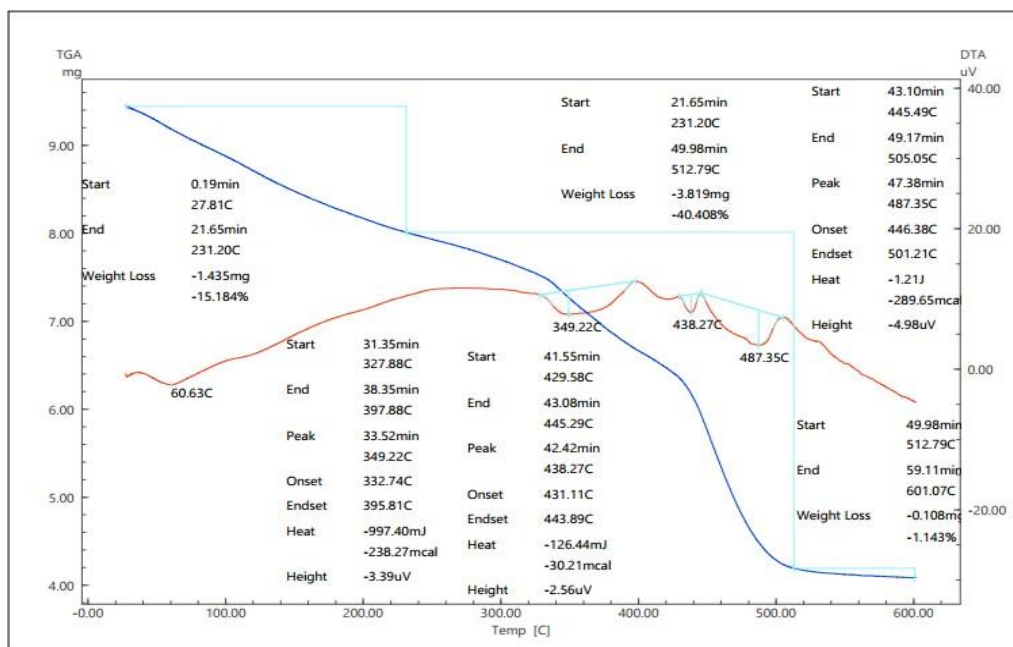


Fig. 7. Thermal analysis superabsorbent hydrogel ((St/CTS)-g-PAA)

## CONCLUSION

It was found that the superabsorbent hydrogel obtained on the basis of starch and chitosan hybrids is more resistant to saline, acidic and alkaline environments and has better morphological properties than hydrogels obtained from starch or chitosan. Also, it was found that the hydrogel obtained on the basis of a hybrid of polysaccharides is more effective than other types of hydrogels due to its high water absorption in distilled and saline water, long-term retention of water in the soil, and water evaporation properties. During the research, it was found that the hydrogel (St/CTS)-g-PAA absorbs water and after the evaporation process is repeated 5-6 times, its water absorption decreases. The main feature of this synthesized superabsorbent hydrogel is to retain, conserve and return water to the roots of plants when needed. This property helps to improve the quality of the soil, prolong the life of plants, increase the growth of plants and their productivity.

## ACKNOWLEDGMENT

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

## REFERENCES

- i. H. Omidian, K. Park, Introduction to hydrogels, in: R.M. Ottenbrite (Ed.), Biomedical Applications of Hydrogels Handbook, Springer, London, UK, 2010, pp. 1–16.
- ii. X. Zhou, H.A. Essawy, M.F. Mohamed, H.S. Ibrahim, N.S. Ammar. Grafting polymerization of acrylic acid

- onto chitosan-cellulose hybrid and application of the graft as highly efficient ligand for elimination of water hardness: Adsorption isotherms, kinetic modeling and regeneration.
- iii. Journal of Environmental Chemical Engineering 6(2018) Pages 2137-2147. doi.org/10.1016/j.jece.2018.03.022.
- iv. H.A. Essawy, H.S. Ibrahim, Synthesis and characterization of poly(vinylpyrrolidone-co-methylacrylate) hydrogel for removal of heavy metal ions from water, React. Funct. Polym. 61(3).(2004). 421–432. doi.org/10.1016/j.reactfunctpolym.2004.08.003.
- v. Kholnazarov B.A., Turayev Kh.Kh., Dzhaliilov A.T. Synthesis of starch, acrylamide, acrylic acid and montmorillonite-based superabsorbent polymer composite. Austrian Journal of Technical and Natural Sciences, 2019, no. 5-6, pp. 69-73.
- vi. M. Sadeghi, H. Hosseinzadeh, Synthesis and swelling behavior of starch-poly(sodium acrylate-co-acrylamide) superabsorbent hydrogel, Turk. J. Chem. 32 (2008) 375–388.
- vii. C. Yu, T. Hui-min, Crosslinked carboxymethylchitosan-g-poly (acrylic acid) copolymer as a novel superabsorbent polymer, Carbohydr. Polym. 341 (2006) 887 –896. doi: 10.1016/j.carres.2006.01.027.
- viii. Y. Zheng, J. Zhang, A. Wang, Fast removal of ammonium nitrogen from aqueous solution using chitosan-g-poly(acrylic acid)/attapulgit composite, Chem. Eng. J. 155(2009)215–222. doi.org/10.1016/j.cej.2009.07.038.
- ix. J. Liu, Q. Wang, Synthesis and characterization of chitosan-g-poly(acrylic acid)/ sodium humate

- superabsorbent, Carbohydr. Polym. 70 (2007) 166–173. doi.org/10.1016/j.carbpol.2007.03.015.
- x. L. Wu, M. Liu, Preparation and properties of chitosan coated NPK compound fertilizer with controlled release and water retention, Carbohydr. Polym. 72 (2008) 240–247. doi.org/10.1016/j.carbpol.2007.08.020.
- xi. S. Hua, A. Wang, Synthesis, characterization and swelling behaviors of sodium alginate-g- poly(acrylic acid)/sodium humate superabsorbent, Carbohydr. Polym. 75 (2009).79–84. doi.org/10.1016/j.carbpol.2008.06.013.
- xii. Pourjavadi, A.M. Harzandi, H. Hosseinzadeh, Modified carrageenan, 3. Synthesis of a novel polysaccharide-based superabsorbent hydrogel via graft copolymerization of acrylic acid onto kappa-carrageenan in air, Eur. Polym. J. 40 (2004) 1363–1370. doi.org/10.1016/j.eurpolymj.2004.02.016
- xiii. Spagnol, F.H.A. Rodrigues, A.G.B. Pereira, A.R. Fajardo, A.F. Rubira, E.C. Muniz, Superabsorbent hydrogel composite made of cellulose nanofibrils and chitosangraft-poly (acrylic acid), Carbohydr. Polym. 87(2012) 2038–2045. https://doi.org/10.1016/j.carbpol.2011.10.017.
- xiv. Kholnazarov. B.A, Turaev, Kh. Kh., Jalilov, A. T. “Synthesis of hydrogels based on cotton cellulose, urea and acrylic acid”. ISJ Theoretical & Applied Science. (2021). 11 (103), 1077-1083. Soi: http://s-o-i.org/1.1/TAS-11-103-121.
- xv. Hisham A. Essawy, Mohamed B.M. Ghazy, Farag Abd El-Hai, Magdy F. Mohamed Superabsorbent hydrogels via graft polymerization of acrylic acid from chitosan-cellulose hybrid and their potential in controlled release of soil nutrients. International Journal of Biological Macromolecules 89 (2016) 144–151. doi.org/10.1016/j.ijbiomac.2016.04.071.
- xvi. Kang Zhong, Zuan-Tao Lin, Xi-Liang Zheng, Gang-Biao Jiang, Yu-Sheng Fang, Xiao-Yun Mao, Zong-Wen Liao. “Starch derivative-based superabsorbent with integration of water-retaining and controlled-release fertilizers”, Carbohydrate Polymers 92 (2013) 1367–1376. doi.org/10.1016/j.carbpol.2012.10.030.
- xvii. Hongkai Zhao, Kehan Zhang, Shoupeng Rui, and Peipei Zhao. “Study on microcr ystalline cellulose/chitosan blend foam gel material”. Sci Eng Compos Mater 2020; 27:424–432. https://doi.org/10.1515/secm-2020-0047.