RJC

RASĀYAN J. Chem.
Vol. 17 | No. 3 |848-854| July - September | 2024
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

HYDROGEL BASED ON STARCH, ACRYLAMIDE AND KAOLINE

A.A. Bolysbek[1], A. Azimov[2], G. M. Iztleuov ✉,[3], A. T. Djalilov[4] and Sh. D. Shirinov[5]

[1]Department Chemical Technology of Inorganic Substances, M. Auezov South Kazakhstan University, Tauke Khan Street.5, 16000, Shymkent, Kazakhstan

[2]Research Laboratory of Innovative Water Purification Systems, M. Auezov South Kazakhstan University, Tauke Khan Street.5, 16000, Shymkent, Kazakhstan

[3]Department of Ecology, M. Auezov South Kazakhstan University, Tauke Khan Street 5, 16000, Shymkent, Kazakhstan

[4]Director of the State Unitary Enterprise "Tashkent Research Institute of Chemical Technology" Tashkent, Uzbekistan

[5]Tashkent Research Institute of Chemical Technology LLC, Republic of Uzbekistan,

✉Corresponding Author: iztileuov.gani@inbox.ru

ABSTRACT

The reduction of water resources in Central Asia forces agriculture to switch to water-saving technologies in the future. One of the ways of rational use of water resources is the use of highly swelling polymer hydrogels (HSP). A hydrogel based on starch, acrylamide, and kaolin was obtained based on a radical copolymerization reaction. In these studies, a superabsorbent composite was synthesized, obtained by the reaction of grafted copolymerization of acrylamide and potato starch in a ratio of 2:1, based on starch, acrylamide, and kaolin. Studies have shown that a superabsorbent composite with the best properties was obtained using 1 wt. % potassium persulfate, 0.8 wt. % methylene bisacrylamide and 2 wt. % aqueous kaolin solution. The rate of swelling of the hydrogel was determined, and it was shown that the moisture absorption of the hydrogel reached 890 g. This proposed method of producing super absorbent composites using natural resources such as starch, and kaolin, of course, reduces the cost of production and also makes the material environmentally friendly.

Keywords: Hydrogel, Hydrolyzed Starch, Acrylamide and Kaoline, Polymerization, Polymers.

RASĀYAN *J. Chem.*, Vol. 17, No.2, 2024

INTRODUCTION

One of the goals of sustainable development is to ensure the availability and rational use of water resources and sanitation for all.[1-2] Reductions in water resources in Central Asia are forcing agriculture to switch to water-saving technologies in the future.[3-4] One of the ways of rational use of water resources is the use of highly swelling polymer hydrogels (HSV).[5-6] Currently, scientists are conducting scientific research in order to obtain new polymer hydrogels based on starch copolymers. These studies require the production of highly efficient hydrogels by copolymerization of polysaccharides and acrylic monomers with certain physical and chemical characteristics, as well as the development of technology for producing hydrogels, which will save water resources when used in agriculture.[7-8] At the same time, it becomes important to create highly efficient and environmentally friendly technologies for the production of highly swelling hydrogels used in agriculture based on synthesized substances from local raw materials - large-tonnage secondary products of the chemical industry.[9-10] The swelling of hydrogels has been studied by many authors. It is well known that the presence of fixed charges characteristic of polyelectrolyte gels determines the significant swelling of the polymer in water.[11-13] This behavior is due to the Donnan equilibrium established between the gel and the external solution, the ionic strength of which strongly affects the degree of swelling.[14-15] Yin and co-authors synthesized super porous hydrogels (CNG) containing poly (acrylicic acid-acrylamide)/O-carboxymethylchitosan, interpenetrating polymer networks by crosslinking Ocarboxymethylchitosan (O-CMX) with glutaraldehyde (GA). The swelling behavior of LNG-PP depended on the content O-CMX, the number of HA and the stitching time.[14-17] Polysaccharides are the main source for the production of biologically based hydrogels. Many studies have used polysaccharides such as starch, carboxymethylcellulose (CMC), alginate and chitosan. Starch is the most commonly used polysaccharide material in the production of hydrogels. Cellulose is the most abundant renewable resource on earth. It is expected to become the main chemical resource in the future.[18-19] Moreover, numerous new functionalities from cellulose are being developed for a wide range of applications due to the growing demand for environmentally friendly and biocompatible products.[18-19] Cellulose, which has a large number of hydroxyl groups, can be easily used to produce hydrogels with gripping structures and properties. Furthermore, cellulose is an environmentally friendly and inexpensive hydrogel that will become a viable substitute for petroleum-based materials in the near future. Superabsorbent hydrogens can absorb more water than conventional water-absorbing materials. Starch mainly reacts with radical polymerization with polyacrylonitrile (PAH), poly (acrylic acid), poly (acrylamide), various binders and initiator.[20-21] Starch-based hydrogels are produced to reduce the use of synthetic hydrogels on the environment. Biological hydrogels can be easily destroyed, so biological hydrogels have been extensively studied in recent years as a replacement for synthetic hydrogels. Polysaccharides are the main source for producing hydrogels on a biological basis. Many studies have used polysaccharides such as starch, carboxymethylcellulose (KMC), alginate and chitosan. Starch is the most commonly used polysaccharide material in the production of hydrogels.[23-24]The aim of the study is to develop a technology for obtaining natural-climatic and soil conditions that save water and mineral resources, effective, highly swelling agricultural hydrogels based on starch copolymers and also to develop a technology for producing efficient and highly swelling hydrogels based on starch copolymers for natural climatic and soil conditions that save water and mineral resources in agriculture.

EXPERIMENTAL

Method for Studying the Degree of Water Absorption

The water absorption capacity of hydrogels was studied in distilled water at room temperature. The hydrogel was taken from the water after it had swelled. The water absorption capacity of the hydrogel (QH_2O) was determined using the equation:[25-27]

$$QH_2O = (m_2-m_1)/m1$$

Where m_1 and m_2 are the weight of the hydrogel in the dry and swollen state.

Starch $(C_6H_{10}O_5)n$ - used corn starch of «Golden Corn» Tashkent starch plant. solid, white powder, molar mass: 162.141* n g/mol, dense: 1.5g/cm^3

Kaolin - the production complex of «Angren Kaolin» LLC was used. The only kaolin enrichment factory in Central Asia is located in Angren, Tashkent Oblast, Republic of Uzbekistan. LLC «Angren Kaolin» produces: - kaolin AKF- 78, - kaolin AX-30, - kaolin ACT-10. Kaolinite and minerals of the kaolinite group (knurled, dickite, galloisite) have a layered structure. Each of the layers consists of one silicone-native tetrahedral mesh and one alumino-oxygen-hydroxyl octahedral mesh, aligned into a single layer so that the vertices of the tetrahedra adjoin the vertices of the octahedra

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a technique used to study the reaction of polymers when heated. DSC can be used to study crystalline polymer melting or glass transition. The DSC setup consists of a measuring chamber and a computer. The two cups are heated in the measuring chamber. The first cup contains the material under study, and the second, as a rule, is empty and is used as a standard. A computer is used to control the temperature and regulate the rate at which the temperature of the cups changes.[26-27]

Study of the Structure of Composite Materials Using IR Spectroscopy

IR spectroscopy is a branch of spectroscopy, that includes the acquisition, study, and application of emission, absorption, and reflection spectra in the infrared region of the spectrum. IR spectra (SHIMADZU IRAFFINITI device1, Japan) were taken from films of composite samples with a thickness of about 12 μm. The IR spectrum of the highly swelling hydrogel shows absorption bands corresponding to functional groups attached to the monomer units.[20-21]

Vol. 17 | No. 3 |848-854| July - September | 2024

Scanning Electron Microscopy (SEM)

The study of phase morphology and structure changes depending on the production conditions and the type of additives was carried out using a scanning electron microscope from Jeol Interactive Corporation, Japan JSM-6460LA

Differential Thermogravimetric Method of Analysis

The synthesized compounds were studied by differential thermogravimetric analysis using a derivatograph system Paulik F, Paulik I, Erdey L. The method is based on changes in thermal effects when heating compounds in the temperature range 293 - 793 K at a temperature rise rate of 2 - 5 K/min.[22-23]

RESULTS AND DISCUSSION

It is known that to study the structural features of polymers, and their water absorption capacity is studied. Water is the active sorbent in most hydrophilic polymer materials, and the pores of the sorbent also play a role in water sorption. When persulfate is heated, sulfate anionic radicals react with water to form free radicals. Free radicals combine hydrogen from the hydroxyl groups of starch. Oxygen then binds to acrylamide and free radical polymerization between starch and acrylamide begins. Methylene bis-acrylamide is added to the reaction to cross-link the high molecular weight composite that binds the polymer chains of the hydrogel identification. The IR spectra of kaolin powder and starch/acrylamide/kaolin composite are shown in Fig.-1(a) and (b). In a layered silicate structure, bands of OH groups can be absorbed at 3687–3618 cm^{-1}. The band observed at 1660 cm -1 can be attributed to bending vibrations of the carbonyl groups of the acrylate unit. In Fig.-1b shows that two new absorption peaks appear in the spectra of the composite at 1398 and 1556 cm-1. Since the characteristic absorption peak of the OH groups on kaolin, starch, and the amide group of $CONH_2$ changed after the copolymerization reaction, it is suggested that the reaction between the OH groups on kaolin, starch, and the CONH2 group of the acrylamide chain occurs, resulting in the formation of a network structure and a water-absorbing group. According to the crosslinking mechanism, it can be assumed that the hydroxyl groups of starch react with the functional groups -CHO and COH based on the initiator, and copolymerization occurs between them. The cross-linking reaction between the polymer chain and the kaolin particle results in the formation of a three-dimensional network, and the cross-linking is also formed based on the cross-linking agent ($CH_2=CH_2-CO-NH-CH_2-NH-CO-CH=CH_2$). The hydrogel is formed by the copolymerization reaction of starch, acrylamide, and ultrafine mineral powder. Since the water absorption capacity of the hydrogel depends on the amount of kaolin, it can be assumed that the kaolin particles, mainly in the form of a cross-linking point, are chemically bonded to the polymer.

Infrared Spectra(s)

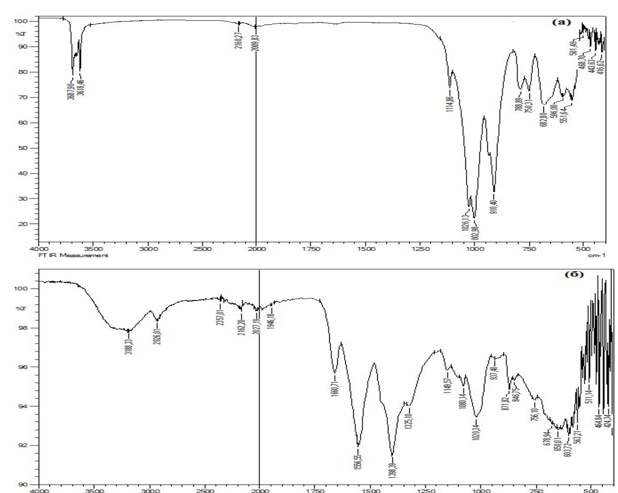


Fig.-1: Infrared Spectra of (a) Kaolin, (b) PAA/Starch/Kaolin Hydrogel

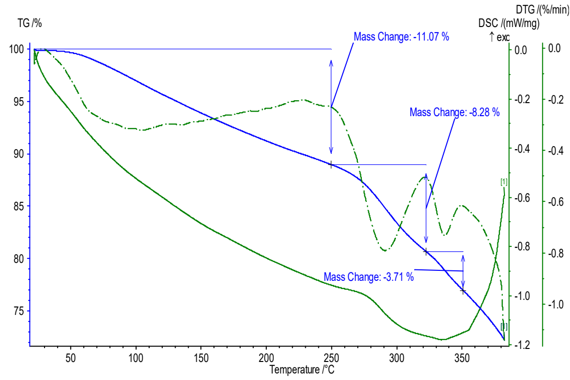


Fig.-2: Differential Thermogravimetric Analyses of Hydrogel Based on AA/Starch/Kaolin

The effect of the content of the amount of initiator and crosslinking agent on the water absorption of powdered composites is shown in Fig.-3 and 4. The water absorption of the hydrogel is 890 g/g at a content of 1 wt% initiator. It can be assumed that water absorption increases to the greatest extent when using an initiator within 1 wt.%. As shown in Fig.-4, water absorption increases with increasing crosslinking agent content from 0.4 to 0.8 wt.% and is 890 g/g at 0.8 wt.% crosslinking agent. In a layered silicate structure, bands of OH groups can be absorbed at 3687–3618 cm^{-1}. The band observed at 1660 cm^{-1} can be attributed to bending vibrations of the carbonyl groups of the acrylate unit. This sample is significantly different from the previous sample - a sharp drop in mass and corresponding peaks on the DSC curve are not visible (Fig. 2). The mass decreases gradually, possibly due to the polymerization reaction (based on acrylamide), and the sample, when heated, behaves like a polymer - approximately three sections of mass loss are observed: the first - 70 - 250 ° C (Δm = -11.07%), the second section 250 - 320oC (Δm=-8.28%) and the third 320-350oC (Δm=-3.71%). Further, the sample also continues to lose weight, but this is already beyond the measurement limit of the device. The maximum rate of destruction at Tmax = 290.6°C is 0.8% per minute.

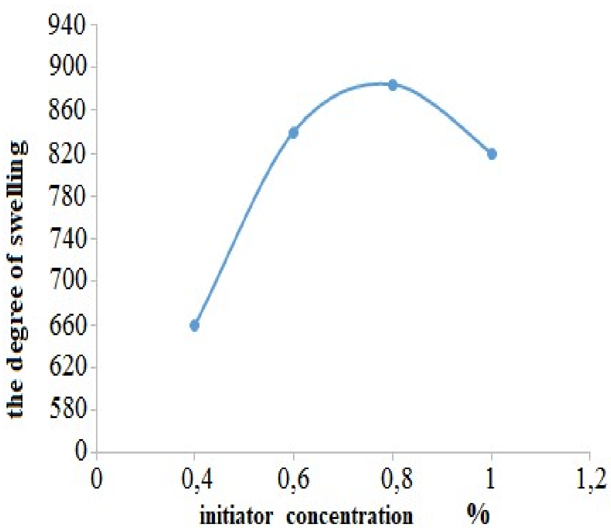


Fig.-3: Effect of Initiator Concentration on the Degree of Swelling of Hydrogels

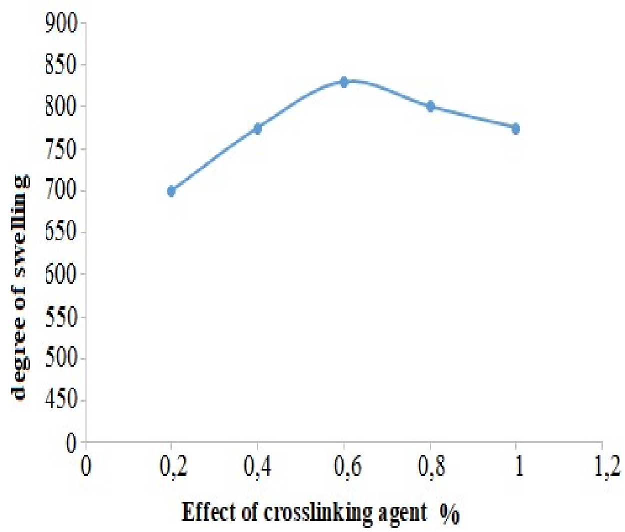
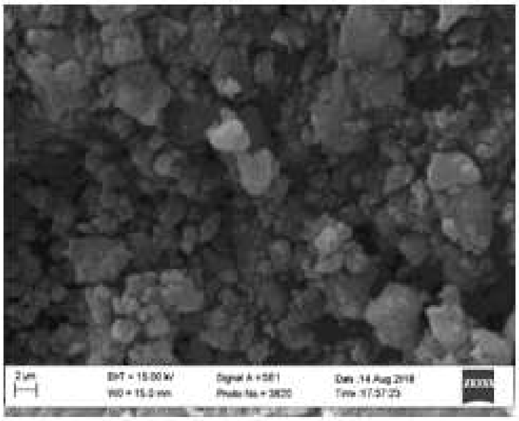
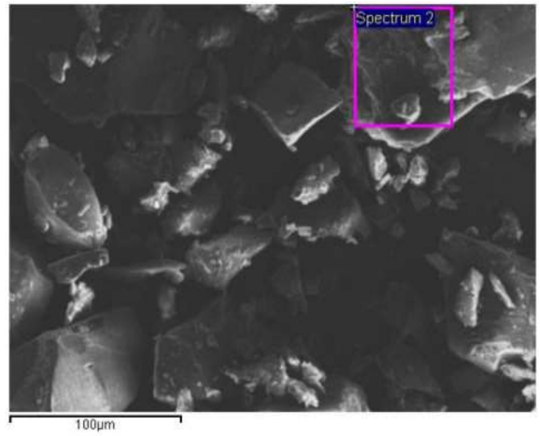


Fig.-4: Effect of Crosslinking Agent Concentration on the Degree of Swelling of Hydrogels

When studying the patterns of the morphological structure of hydrogels, researchers attach great importance to the use of electron microscopy methods. The mechanism of formation of the porous structure of hydrogels is mainly determined by the nature of the inert diluent (pore formation) and the amount of cross-linking agent in the reaction system. At the same time, elongation of the polymer chain in the early stages of polymerization plays a key role in increasing the uniformity of the morphology of the system. In order to determine the morphological structure of the synthesized hydrogels, their images were studied using a scanning electron microscope (Fig.-5).


(a)



(b)

Fig.-5: SEM Image of Kaolin (a), Image of the Starch/AA/K Composite (b)

The unreacted kaolin components are evenly distributed in the polymer matrix scanning electron microscopy images of minerals and composite materials, shown in Fig.-5. As can be seen from the above figures, the synthesized sorbents have a gel structure, which contains micropores on the surface.

Элемент	Весовой %
C	43.35
N	4.14
O	39.8
Na	8.56
Mg	0.22
Al	0.13
Si	0.31
S	0.09
Cl	0.7
K	0.06
Ca	3.12

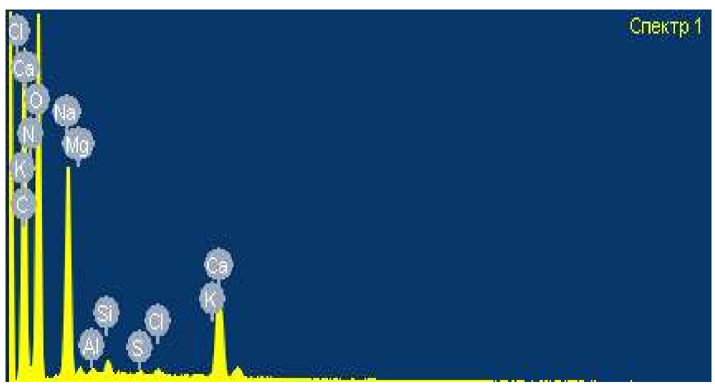


Fig.-6: Elemental Analysis Data for Cr/AA/K Hydrogels

In the synthesis of hydrogels, added kaolin, which contains silica, promotes the binding process during polymerization, increasing the molecular weight of the polymer and increasing its mechanical strength and thermal stability. Also, added minerals improve the properties of hydrogels, such as water absorption and water retention, but also lead to lower costs. Due to the fact that if the amount of kaolin is increased, the small number of additional oxides in the kaolin will affect the binding points of the polymer chain, resulting in a decrease in the molecular weight of the polymer. At the same time, the water absorption of the hydrogel also decreases. As the ions in solutions increase, the density of the solution also becomes high, and the degree of swelling of the hydrogels decreases. Figure-7 shows the effect of salt solutions on the water absorption of the hydrogel; it can be seen that with increasing concentration of table salt in the solution, the swelling of the hydrogel decreases.

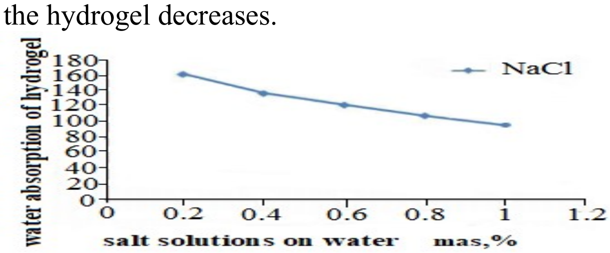


Fig.-7: Effect of Salt Solutions on Water Absorption of Hydrogel

Water absorption in a 1% NaCl solution is 165 g/g. We have synthesized a superabsorbent composite, synthesized by the graft copolymerization reaction of acrylamide and potato starch in a 2:1 ratio, based on starch, acrylamide, and kaolin. Research has shown that the superabsorbent composite with the best properties was obtained using 1 wt.% potassium persulfate, 0.8 wt.% methylene bis-acrylamide, and 2 wt.% kaolin aqueous solution.

CONCLUSION

Influence of various factors at the synthesis of hydrogels and infrared spectral characteristics of their structure results. As a result of the analysis of infrared spectral analysis of the obtained hydrogels, approximate structural formulas of polymers have been determined. The obtained drawings on scanning electron microscopes for the determination of the morphological structure of synthesized hydrogels have been investigated. The porosity and swelling characteristics of hydrogels are shown. Chemical stability of synthesized sorbents in different corrosive media. On the basis of the obtained data in experiments on the thermal stability of studied sorbents, exothermic and endothermic effects observed by mass change as a result of polymer destruction during sorbent heating are analyzed with the help of derivative analysis. In synthesized sorbents, the dependence of water sorption on pH value is investigated, and the obtained data are shown in the form of a graph. Studies have shown that a superabsorbent composite with the best properties was obtained using 1 mass. % potassium persulfate, 0.8 mass. c. Methylene bis-acrylamide and 2 mass % aqueous kaoline solution. The hydrogel swelling rate has been determined and the hydrogel moisture absorption has been shown to reach 890g. This approach to the production of super absorbent composites using natural resources such as starch, and kaolin, certainly reduces the cost of production and also makes the material environmentally friendly. The above results show that the composite exhibits excellent complex absorbent properties.

ACKNOWLEDGEMENTS

The research work was carried out based on project No. 414-PCF-23-25 dated November 15, 2023, subject: BR21882218 «Development and implementation of new highly efficient moisture- and resource-saving technologies that increase crop yields and modernize the agro-industrial complex» financed by Ministry of Science and Higher Education of the Republic of Kazakhstan.

CONFLICT OF INTERESTS

All the authors declare having no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

A.A.Bolysbek http://orchid.org/0000-0001-8708-2608
A. Azimov http://orchid.org/0000-0002-1316-5854
G.M. Iztleuov http://orchid.org/0000-0002-5722-342X
Sh.D.Shirinov http://orchid.org/0009-0003-0886-8365
A.T. Djalilov https://orcid.org/0000-0002-1949-5790

REFERENCES

1. A. Azimov, L. Nekrasova, D. Gur, *Journal of Water and Land Development*, **52(I–III)**, 34(2022), http://dx.doi.org/10.24425/jwld.2021.139941
2. A. Yessenbek, M. Satayev, A. Azimov, *Water Practice & Technology,* **18(3),** 563(2023), http://dx.doi.org/10.2166/wpt.2023.018

3. Zh. A. Shingisbaeva, G.M. Iztleuov, A.A.Abduova, A.S. Taubayeva, Zhorabaeva, *Izvestiya Vysshikh Uchebnykh Zavedenii, Seriya Teknologiya Tekstil'noi Promyshlennos*ti, **379(1),** 323(2019).
4. K. Daniel , A.Iskandar , B. Bazartseren , B. Dietrich, C. H. Sergey, J. Jerker, L. Lanhai, A. Jeffrey, *Environmental Earth Sciences*, **690**, 76(**2017),** http://dx.doi.org/10.1007/s12665-017-6994-x
5. M. Satayev, A. Azimov, G. Iztleuov, L. Satayeva, *Water*, **16(1),** 172(2024), http://dx.doi.org/10.3390/w16010172
6. B.M. Smailov, A.S Tleuov, O.K. Beisenbayev, S.T. Tleuova, M.M. Yeskendirova, B.A. Userbaeva, *Rasayan Journal of Chemistry*, **15(2)**, 1085(2022), http://dx.doi.org/10.31788/RJC.2022.1526806
7. I. DAbbazov, R. Kaldybaev, G. Bektureyeva, G. Izteuov, A. Kolesnikov, *Polish Journal of Environmental Studies*, **32(4),** 3007(2023), http://dx.doi.org/10.15244/pjoes/163341
8. X. Xie, and Q.Liu, *Starch/Starke,* **56,** 364(2004), http://dx.doi.org/10.1002/star.200300261
9. X. Song, F. Chen, Sh. Liu, *BioResources.* **11(3),** 6378(2016), http://dx.doi.org/10.15376/biores.11.3.6378-6392
10. M.K. Włodarczyk-Biegun, K. Farbod, M.W.T. Werten, C.J. Slingerland, F.A. de Wolf, van den J..P. Beucken, *PLoS ONE* **11(5),** e0155625(2016) https://doi.org/10.1371/journal.pone.0155625
11. F. Marzieh, B. Jaleh, A.Ayuob, O. Yadollah, *BioImpacts***.,** **5(4),** 159(2015). http://dx.doi.org/10.15171/bi.2015.31
12. M. Kozicki, M. Kołodziejczyk, M. Szynkowska, *Carbohydrate Polymers*, **140**, 74(2016), http://dx.doi.org/10.1016/j.carbpol.2015.12.017
13. H. Shekofteh, N.Salari, *Desert,* **21(1),** 91(2016), http://dx.doi.org/10.22059/JDESERT.2016.58322
14. M.A. Navarra, Dal Bosco, M.Chiara, , S. Judith, F.M. Vitucci, A.Paolone, S.Panero, *Membranes,* **5(4),** 810(2015), http://dx.doi.org/10.3390/membranes5040810
15. A. A. L.Gonçalves, A.C.Fonseca, I.G.P. Fabela, J.F.J. Coelho, A.C. Serra, *Express Polymer Letters,* **10(3),** 248(2016). http://dx.doi.org/10.3144/expresspolymlett.2016.23
16. H. I. Ozgunduz, H.G. Kandilci, N. Acarali, H. Sarac, *Journal of Engineering & Natural Sciences*, **34(1**), 115(2016).
17. W. Xiaoxiang, B.Dengshan, Ch. Mingjie, Zh. Aiping, L. Chuanfu, S. Runcang, *BioResources,* **10(4**), 8339(2015). http://dx.doi.org/10.15376/biores.10.4.8339-8351
18. B. Tamanna, *Monomers and Polymers*, **7(1),** 311(2004), http://dx.doi.org/10.1163/1568555041475329
19. U. Akhmedov, O. Tanatarov, A. Usmonova, M. Abramatov, *E3S Web of Conferences,* 390(2023). http://dx.doi.org/10.1051/e3sconf/202339005031
20. B. H. Hu, P.B. Messersmith, *Orthod Craniofac Research*, **8(3),**145(2005), http://dx.doi.org/10.1111/j.1601-6343.2005.00330.x.
21. A. Pastoriza, I.Pacios, *Polymer Science*, **23(8**), 1205(2005), https://doi.org/10.1002/pi.1832
22. A.A. Kamshybaev, G.M. Iztleuov, P.S. Sultanbekova, A.A. Abduova, G.M. Nurmasheva, Y.K. Yessimov, *Rasayan Journal of Chemistry*, **Special Issue**, 233(2022), http://dx.doi.org/10.31788/RJC.2022.1558200
23. B.A.Kholazarov, H.H.Tshraev, S.D. Shirinov, A.T. Jalilov, "Synthesis of superabsorbent hydrogel based on starch, acrylic acid and montmorillonite", Universum: Technical Sciences, Mockwa 8/65 August 2019, pp. 13-16
24. B.A.Kholazarov, H.H. Tyraev, A.T. Jalilov, Sh.D. Shirinov, "Research of a new hydrogel synthesized on the basis of starch, acrylamide and bentonite", *Universum: Technical sciences,* **4(61**),53(2019)
25. M.B. Yunussov, A.M. Yessirkepova, T.N. Mashirova, S.Z.H. Rysbayeva, Z.H.A. Sarieva, *Izvestiya Vysshikh Uchebnykh Zavedenii, Seriya Teknologiya Tekstil'noi Promyshlennosti*, **387(3**), 36(2020).
26. P.Zh Tozhiev Development of technology for obtaining highly filled polyolefins based on local raw materials. *Technical Sciences*; Termez-2019. P.61.
27. B.A. Kholnazarov, H.H.Turaev, A.T Jalilov, *Navoi, November* **22,** 36-38(2018).

[RJC-8844/2024]