

# Potato starch copolymers as superabsorbents of methylene blue from aqueous solutions

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## ABSTRACT

Superabsorbent materials based on potato starch (St) grafted polyacrylamide (PAM) were synthesized by radical polymerization with ammonium persulfate as initiator. The N,N'-methylenebisacrylamide (MBA) was a cross-linking agent. Starch grafted polyacrylamides (St-g-PAM) and their hydrolyzed analogues were specified by X-Ray Diffraction, Fourier transform infrared spectroscopy, differential scanning calorimetry and thermal analysis. The studies confirmed the grafting of PAM into the starch backbone and partial alkaline hydrolysis of PAM. The sorption of methylene blue (MB) from aqueous solutions was investigated depending on the initial concentration of the MB solution, the contact time, the amount of PAM grafted onto starch and the structure of the sorbent (hydrolyzed or non-hydrolyzed material). In the case of non-hydrolyzed material, satisfactory sorption results (adsorption efficiency - 42 mg MB/g of sorbent and swelling mass - 1600% ) were obtained for St-g-PAM with 40 wt.% of PAM (St 40PAM). On the other hand, the best results were achieved for the hydrolyzed material (H St 40PAM): 88 mg MB/g of sorbent and 2100%, respectively.

**Keywords:** starch, polyacrylamide, absorbents, superabsorbent, starch graft copolymers.

## INTRODUCTION

The industrial sector consumes giant amounts of water and as a result generates equally large amounts of sewage. The growth of the world's population and dynamic economic development have a huge impact on the state of environment, and unfortunately also the increase in various types of pollution. These pollutants include substances such as dyes, pesticides, pharmaceuticals, metal cations and others. MB is a cationic dye that is often used in scientific tests due to its intense blue color [1–4]. However, excessive exposure of living organisms to MB can cause jaundice, nausea, dead tissue and rapid heart rate [5]. It is our duty to continuously improve water quality and develop more effective ways of removing pollutants from the environment [6–8]. It is important to link environmental protection to the principles of Green Chemistry or sustainable chemistry, i.e. the design of chemical materials and processes

that reduce or eliminate the consumption or formation of hazardous substances.

Starch is a natural polymer and it is relatively easy to modify, and the obtained starch materials ideally fit into the current directions of scientific research [9–18]. Starch polymers are used in many industrial fields, however, for the purposes of water and sewage treatment, it is possible to use starch flocculants [19–21] and starch sorbents [22–24]. Superabsorbent polymers (SAP) are cross-linked polymers that have the ability to retain liquid/water many times more than their dry weight [25]. SAPs are divided into two basic groups: petroleum-based SAP - derived mainly from acrylic acid and acrylamide monomers, and SAP based on natural polymers [26, 27]. The sorption efficiency of starch SAPs can be regulated and adjusted to the environmental conditions. The sorption properties of SAP (adsorption or swelling efficiency) depend, among others, on the cross-linking density [28–31], the type of

cross-linking agent used [32, 33], the methods of obtaining materials [28–33, 34], the morphology of the material, the polymer structure [28–35], the type of modification of the sorption material, e.g. hydrolysis [36], the reaction time and the initiator used [11, 23, 25, 35].

In this article, the results of sorption efficiency for copolymers of St grafted PAM are presented. Acrylamide starch materials were synthesized in a free radical reaction using N,N'-methylenebisacrylamide as a cross-linking agent. The polymerization initiator was ammonium persulfate. Two series of SAP materials were obtained: starch-g-polyacrylamide with variable PAM content from 10 to 40% by weight and their partially hydrolyzed counterparts. Starch or cross-linked potato starch – St MBA were used as reference materials. The SAP was characterized using fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetry (TGA) and X-ray diffraction (XRD). The results of MB sorption studies from solutions with different concentrations using hydrolyzed and non-hydrolyzed starch graft copolymers were presented. The application studies were supplemented with mass swelling studies after 2 days. The presented results expand the knowledge on the so-called green materials and confirm the possibility of designing a superabsorbent composition for the most effective wastewater treatment.

## MATERIALS AND METHODS

### Materials

Potato starch (super standard quality, St) with moisture content of ca. 16.5 wt.% and 29.7 wt.% of amylose from Potato Industrial Enterprise “Nowamyl” S.A., Poland was used for syntheses. Acrylamide (AM) and N,N'-methylenebisacrylamide (MBA) were purchased from Merck, Germany, in the purity of both (~99%) the monomer and the crosslinker in reaction, respectively. Ammonium persulfate (~99,9%, ASP) from Chempur, Poland was used as the free radical polymerization initiator. Acetone and methanol (analytical reagent grade), sodium hydroxide (~99,9%, NaOH) and methylene blue (~99,9%, MB) were purchased also from Chempur, Poland.

### Polymerization of starch-g-polyacrylamide

The procedure for obtaining copolymers of starch-g-polyacrylamide (St-g-PAM) has been thoroughly presented in the literature [30]. In free radical polymerization, PAM was grafted onto starch and then the copolymer was cross-linked using MBA in 0.5 wt.%. Ammonium persulfate was used based on the weight of AM (1.0 wt.%). A series of starch materials with variable amounts of PAM used in synthesis, from 10 to 40 wt.%, were obtained (from St 10PAM to St 40PAM, respectively). According to literature reports [8, 20, 30, 36], previously gelatinized starch was used for polymerization (30 min at 82 °C). Polymerization was carried out at a nitrogen atmosphere. Starch copolymers were precipitated in excess of acetone. Then, the SAPs were washed with a mixture of distilled water and methanol to clean the material from polyacrylamide. Finally, the cross-linked starch copolymers were dried at 60 °C for 24 hours.

A series of partially hydrolyzed starch-g-polyacrylamide SAPs (H St 10PAM to H St 40PAM) were synthesized by alkaline partial hydrolysis of St 10PAM to St 40PAM, respectively, [36]. For this purpose, at the end of St-g-PAM polymerization, 2 ml of 2 M NaOH solution was added (0.2 wt.% NaOH in the reaction mixture), maintaining the solution at 50 °C for 3 h. Then, the hydrolyzed material was precipitated, washed and dried according to the previously described procedure.

Schematic synthesis of cross-linking starch grafted polyacrylamide and their partially hydrolyzed products is shown in Figure 1.

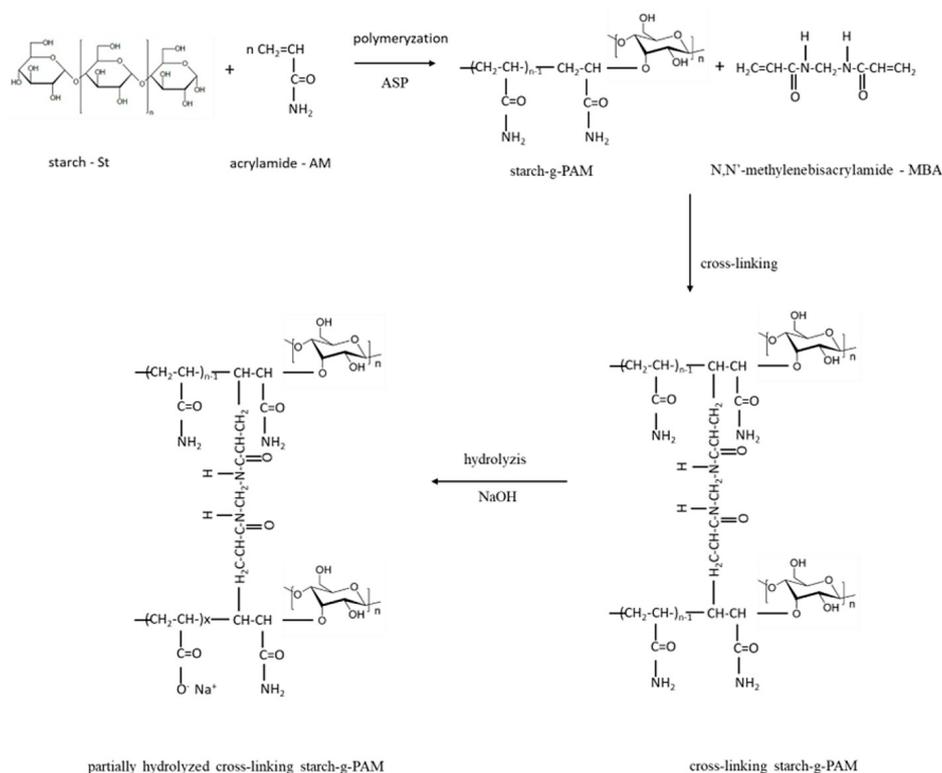
### Methods

#### *Fourier transform infrared (FTIR) spectroscopy.*

FTIR spectra of dried samples were obtained in the range of 500–4000 cm<sup>-1</sup> using a Nexus FTIR spectrometer (Thermo Nicolet Corp., USA) with a Golden Gate (ATR) attachment. The spectra were processed with the OMNIC computer program.

#### *X-Ray Diffraction (XRD).*

Samples of starch copolymers were examined by XRD method. Empyrean X-ray diffractometer, CuK $\alpha$  radiation ( $\lambda = 1.544 \text{ \AA}$ ) (Malvern Panalytical, Malvern, UK) was used.



**Figure 1.** Schematic synthesis of cross-linking St PAM and hydrolyzed H St PAM

### Differential scanning calorimetry (DSC).

DSC of the materials was performed using Q100 DSC (TA Instruments Inc., USA) with a heating rate of 10 °C/min, from 0 to 200 °C in a nitrogen atmosphere. The average sample weight was ~ 5 mg. Hermetically sealed aluminum pans were used.

### Thermogravimetric analysis (TGA)

Thermal properties of starch materials were determined in air using a TA Instruments TGA Q5000. Temperatures from 20 °C to 900 °C were used with a heating rate of 10 °C/min.

### Removal of methylene blue from aqueous solution

Mechanically powdered material 50 mg (< 0.3 mm) was used in the sorption tests. Methylene blue was removed from solutions with concentration of 3, 6 and 10 mg/L. The absorbance changes of MB solutions (50 ml) were determined using a UV-9000 BioSens spectrophotometer at wavelength of 664 nm. The tests were carried out by placing starch samples in the appropriate MB solutions and measuring the changes in absorbance of MB solutions with time. Tests were also conducted after 24 and 48 hours. Sorption tests were

carried out at neutral pH=7.0 The solution purification - MB removal ( $R_{mb}$ ) was determined based on the formula 1:

$$R_{mb} = [(X_0 - X_t) \cdot 100\%]/X_0(\%) \quad (1)$$

where:  $X_0$  – the entrance concentration of MB (mg/L),  $X_t$  – the concentration of MB (mg/L) after time t.

Equation 2 defines the adsorption efficiency (Q), i.e. the amount of MB adsorbed per gram of sorbent (mg/g):

$$Q = [(X_0 - X_t) \cdot V]/D(\text{mg/g}) \quad (2)$$

where:  $V$  – the volume of solution (L),  $D$  – the dry sorbent mass (g).

### The swelling properties.

Mass swelling measurements were made after 48 hours. The swollen material was filtered and weighed. Selected samples were photographed. The mass swelling (W) was calculated using formula 3:

$$W = [(W_t - D) \cdot 100\%]/D(\%) \quad (3)$$

where:  $W_t$  – the mass of swollen sample after time t [g].

Sorption measurements were made three times for one material and the results were averaged.

## RESULTS AND DISCUSSION

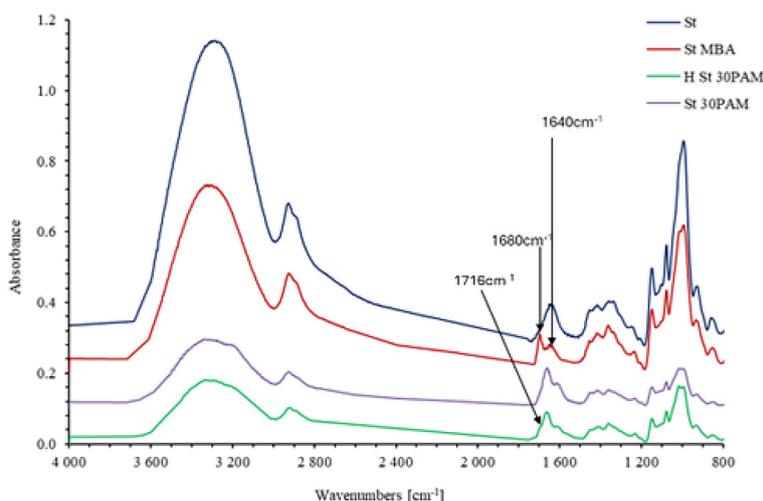
### Material characteristics

Figure 2 shows the FTIR spectra of potato starch (St), cross-linked starch (St MBA), copolymer of starch-g-polyacrylamide with 30 wt.% PAM (St 30PAM) and corresponding hydrolyzed material (H St 30PAM). A typical FTIR spectrum of starch includes: absorption bands at 1015, 1080 and 1160  $\text{cm}^{-1}$  (resulted from stretching vibrations of the C–O–C); at 1380 and 1460  $\text{cm}^{-1}$  (corresponding to bending vibrations of the O–H plane); at 2900  $\text{cm}^{-1}$  (stretching vibrations of the C–H groups and symmetric  $\text{CH}_2$ ) and band in the wavelength range of 3000–3650  $\text{cm}^{-1}$  (stretching vibrations of the –OH). In the spectra of the cross-linked material (St MBA) new adsorption peaks appear at about 1680  $\text{cm}^{-1}$  and 1640  $\text{cm}^{-1}$  (amide I of the –C=O, and amide II of the –N–H), confirming the cross-linking reaction between St and MBA [37]. The FTIR spectra of starch and starch copolymers show a broad band between 3000  $\text{cm}^{-1}$  and 3650  $\text{cm}^{-1}$  (the N–H stretching of PAM overlapping with the –OH stretching of St). The starch grafted PAM samples show three characteristic absorption bands for  $\text{CONH}_2$  at: 1670  $\text{cm}^{-1}$  (C=O), 1610  $\text{cm}^{-1}$  (–N–H) and 1405  $\text{cm}^{-1}$  (–C–N) [38]. These prove the effective implantation of PAM into the starch chains. The confirmation of hydrolysis in H St 30PAM materials is the appearance of a small, new signal at 1716  $\text{cm}^{-1}$  indicating carbonyl stretching of carboxylate ions. Moreover, in the FTIR spectra of H St 30PAM, a

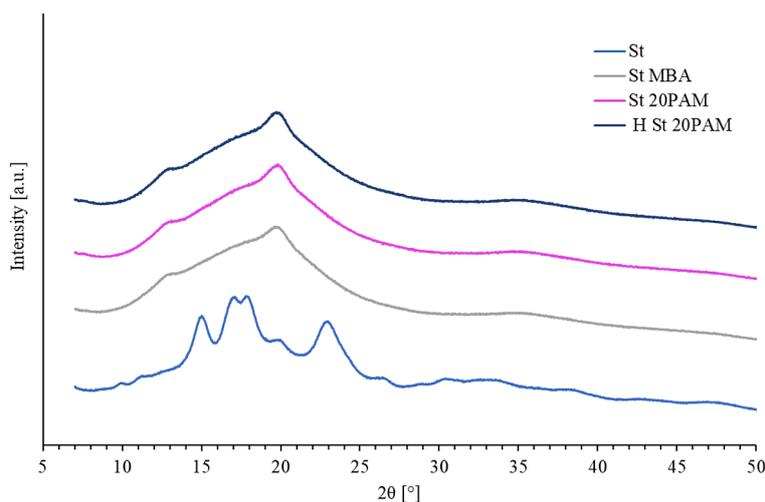
smoothing of the broad band at 3000–3650  $\text{cm}^{-1}$  of the hydroxyl group and the N–H amide group was observed, which confirmed the loss of  $\text{NH}_3$  during hydrolysis [36].

Figure 3 depicts the XRD patterns of starch, cross-linked starch and synthesized SAPs. Starch characterization peaks were at ca.  $2\theta=15^\circ$  (typical of B-type crystal scattering for retrograded starch),  $17^\circ$ ,  $18^\circ$ ,  $20^\circ$ , and  $23^\circ$ . Modified starches (gelatinized, cross-linked, grafted PAM) show one broad diffraction peak from  $2\theta=15^\circ$  to  $2\theta=27^\circ$  with maximum at about  $20^\circ$   $2\theta$  (wide halo appears from MBA and PAM), which indicates the almost amorphous nature of the synthesized polymers. Starch loses its crystallinity during modification. The XRD patterns showed a successful grafting and homogeneous cross-linking as confirmed by the disappearance of starch diffraction peaks [29, 39].

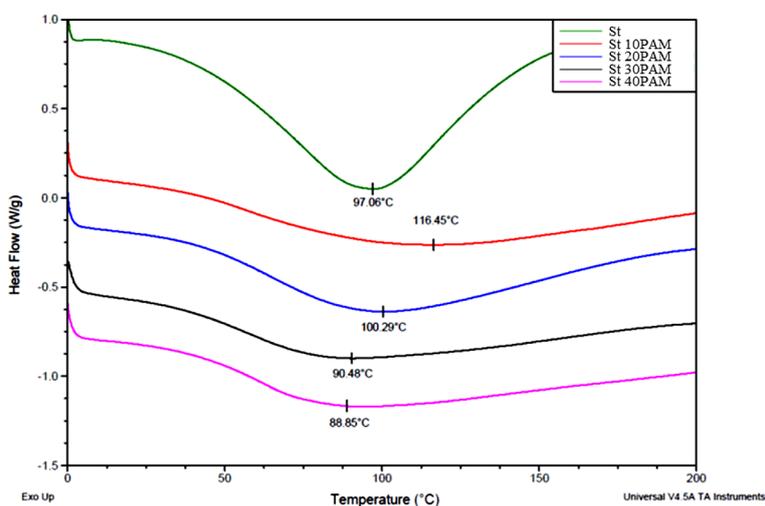
The DSC test results were presented graphically (Figure 4) and tabularly (Table 1). Figure 4 displayed the DSC curves of St and a series of starch copolymers with PAM. All DSC curves showed a similar trend and an endothermic process is observed [37]. The top temperature  $T_{\text{max}}$  for St was 97.06  $^\circ\text{C}$ , and maximum temperatures for the starch-PAM copolymers series were in line with the literature [30]. Shifts of endothermic peaks in the DSC curves towards lower temperatures were observed with increasing PAM content in the absorbent. The same rule applies to the hydrolyzed copolymer series (Table 1), the top temperature for H St 10PAM was 99.23  $^\circ\text{C}$  but for H St 40PAM was 86.18  $^\circ\text{C}$ . The introduction of



**Figure 2.** Fourier-transform infrared spectra of starch (St), cross-linked starch (St MBA), hydrolyzed starch-g-polyacrylamide absorbent with 30 wt.% PAM (H St 30PAM) and corresponding non-hydrolyzed material (St 30PAM)



**Figure 3.** XRD of starch (St), cross-linked starch (St MBA), starch-g-polyacrylamide with 20 wt.% PAM (St 20PAM) and hydrolyzed material (H St 20PAM)



**Figure 4.** Differential scanning calorimetry of potato starch (St) and cross-linked St-g-PAM with 10 to 40 wt.% of PAM (from St 10PAM to ST 40PAM)

**Table 1.** Maximum peak temperatures from DSC studies for starch and starch-g-PAM

Polymer	T <sub>max</sub> [°C]	Polymer	T <sub>max</sub> [°C]
St	97.06	St MBA	94.92
St 10PAM	116.45	H St 10PAM	99.23
St 20PAM	100.29	H St 20PAM	91.91
St 30PAM	90.48	H St 30PAM	87.71
St 40PAM	88.85	H St 40PAM	86.18

hydrophilic carboxyl groups (hydrolyzed PAM) into the St-g-PAM chain causes a decrease in their characteristic temperature due to water-hydrophilic polymer interactions.

Thermogravimetric curves for St and St xPAM series (x = 10 to 40) are shown in Figure 5, while the mass losses of all samples at selected

temperatures 100 °C, 300 °C and 500 °C are given in Table 2. In order to prevent the influence of air humidity, thermal tests of the obtained materials were carried out on previously dried samples. The behavior of starch and starch copolymers under the influence of increasing temperature is similar (almost the same shape of TG curves). Starch

SAPs decomposition can be divided into three stages: the dehydration (30–220 °C), starch destruction (250–350 °C) and the degradation of polyacrylamide (380–620 °C) [10, 31]. It could be observed from the thermogravimetric analysis curves (Figure 5) and TG data for all materials (starches, hydrolyzed and no-hydrolyzed starch copolymers – Table 2) that grafting of starch with synthetic polymers enhanced the thermal stability of SAPs [39]. The mass losses for both series of starch copolymers are lower compared to potato starch and cross-linked starch at both 300 °C and 500 °C.

### Methylene blue sorption

In the adsorption tests, the sorption of methylene blue from aqueous solutions with an initial MB concentration of 3, 6 and 10 mg/L was investigated. The influence of the type sorbents (hydrolyzed and no-hydrolyzed), structure of sorbent (grafted PAM from 10 to 40 wt.%), treatment

time (from minutes to 48h) and initial MB concentration were considered.

Figure 6 illustrates the effect of the initial MB solution concentration and starch cross-linking on the dye removal from the studied system. MB removal from the solution is higher for cross-linked starch compared to native starch for initial dye concentrations of 3 and 6 mg/L, while for the concentration of 10 mg/L the results are comparable. Cross-linking reduces the distance between adjacent polymer chains, making it difficult for substances to penetrate and adsorb [37]. A longer time is needed for the material to swell in its entire volume and allow the substance to penetrate deeper.

The removal of MB from solution with different initial concentration during the first 2 h of tests and the effect of starch graft copolymers composition illustrate on Figure 7 (no-hydrolyzed material) and Figure 8 (hydrolyzed starch SAPs). For both series of starch copolymers, purification of MB solutions is more effective at lower

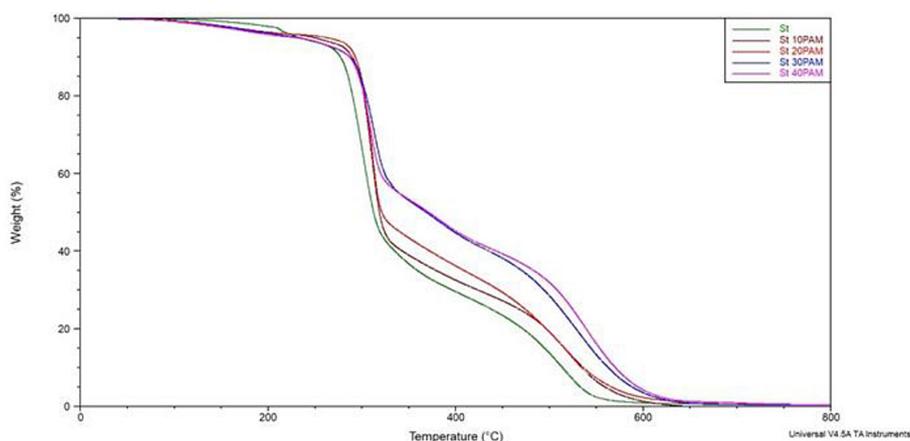
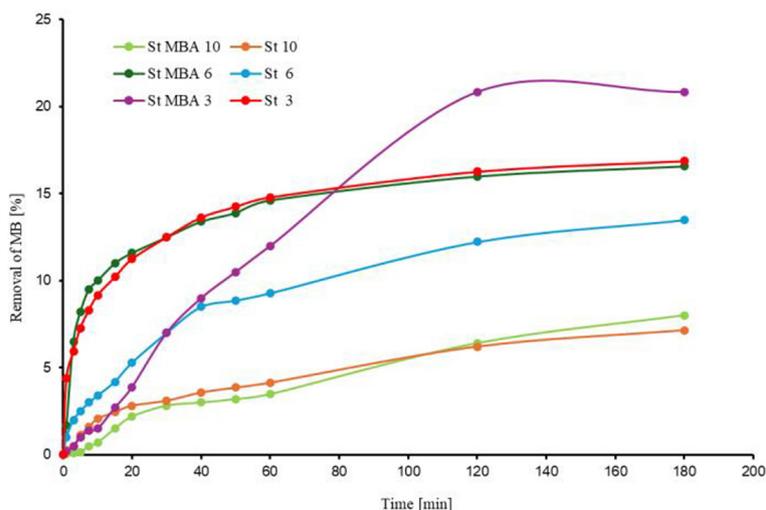


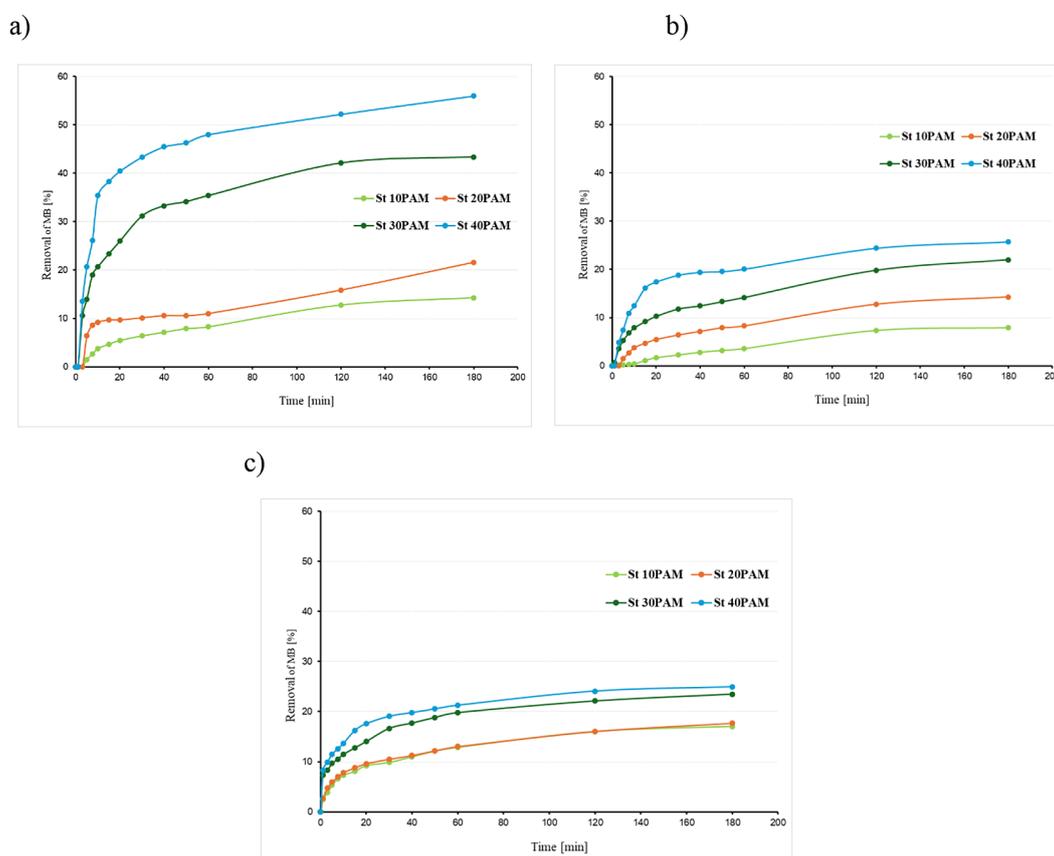
Figure 5. The thermogravimetric curves of starch (St) and cross-linked St-g-PAM with 10 to 40 wt.% of PAM (from St 10PAM to ST 40PAM)

Table 2. Mass loss [%] of samples at selected temperatures 100 °C, 300 °C and 500 °C obtained during thermogravimetric studies

Polymer	100 [°C]	300 [°C]	500 [°C]
St	1	30	86
St MBA	2	35	87
St 10PAM	2	15	80
St 20PAM	2	15	80
St 30PAM	2	15	72
St 40PAM	2	15	68
H St 10PAM	2	30	85
H St 20PAM	2	27	85
H St 30PAM	3	23	80
H St 40PAM	4	25	74



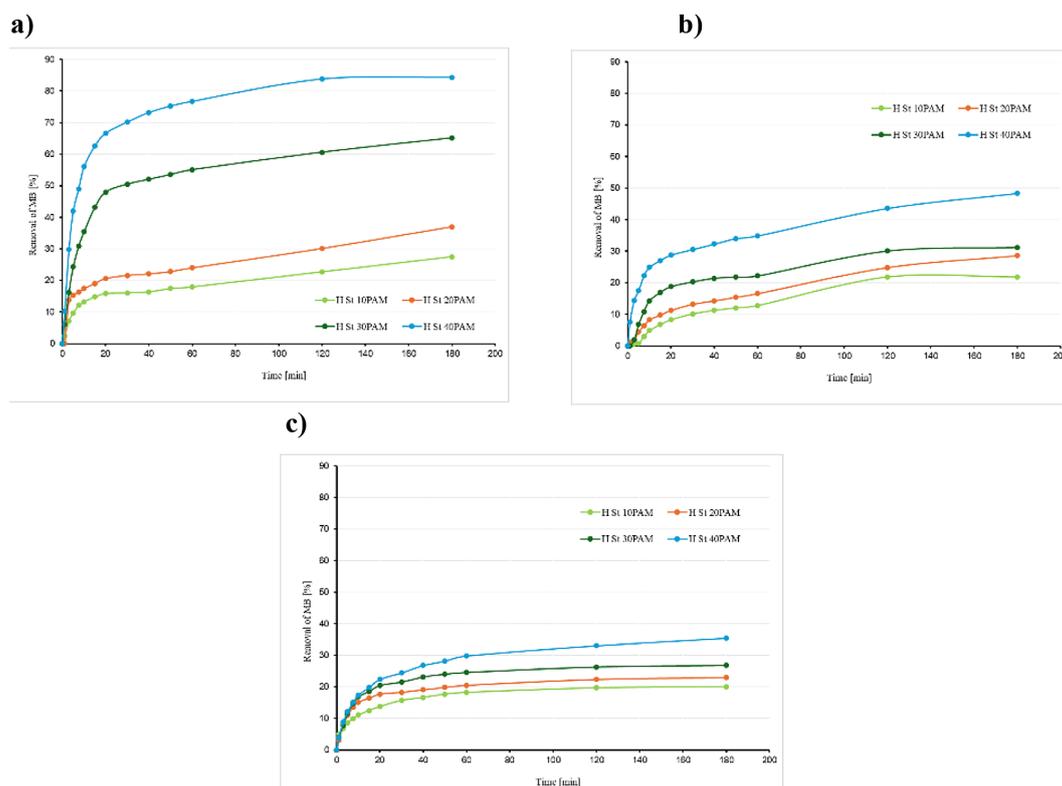
**Figure 6.** The removal of MB in time for starch and cross-linking starch of MB initial concentration 3 mg/L (St 3 and St MBA 3), 6 mg/L (St 6 and St MBA 6) and 10 mg/L (St 10 and St MBA 10)



**Figure 7.** The removal of MB in time of initial concentration a) 3 mg MB/L, b) 6 mg MB/L, c) 10 mg MB/L for starch SAPs with different amount of PAM from 10 to 40 wt.%

concentrations (3 mg/L, 56% for St 40PAM) than in more concentrated MB solutions (10 mg/L, 25% for St 40PAM). Additionally, regardless of the initial solution concentration, purification of the MB solution is more effective with the increase of the PAM content in the starch SAP e.g. 26% for

St 40PAM and 8% St 10PAM (Figure 7b) or 48% for H St 40PAM and 22% H St 10PAM (Figure 8b) [30, 40]. However, the most satisfactory purification results were obtained for the series of hydrolyzed starch copolymers (84% H St 40PAM – Figure 8a, 48% for H St 40PAM – Figure 8b and

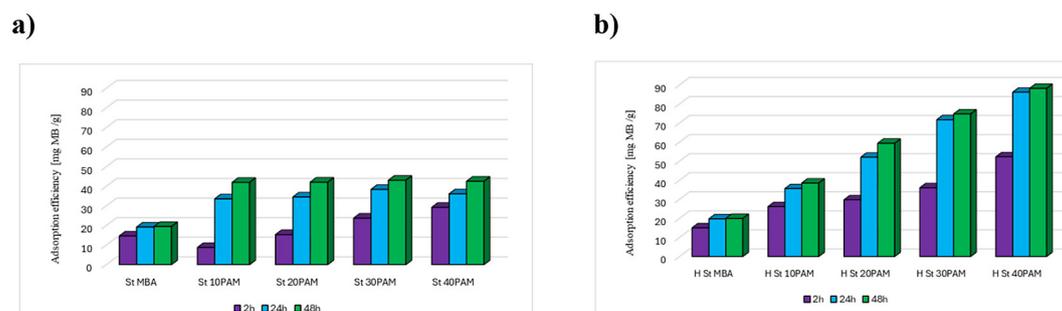


**Figure 8.** The removal of MB in time of initial concentration a) 3 mg MB/L, b) 6 mg MB/L, c) 10 mg MB/L hydrolyzed starch SAPs with different amount of PAM from 10 to 40 wt.%

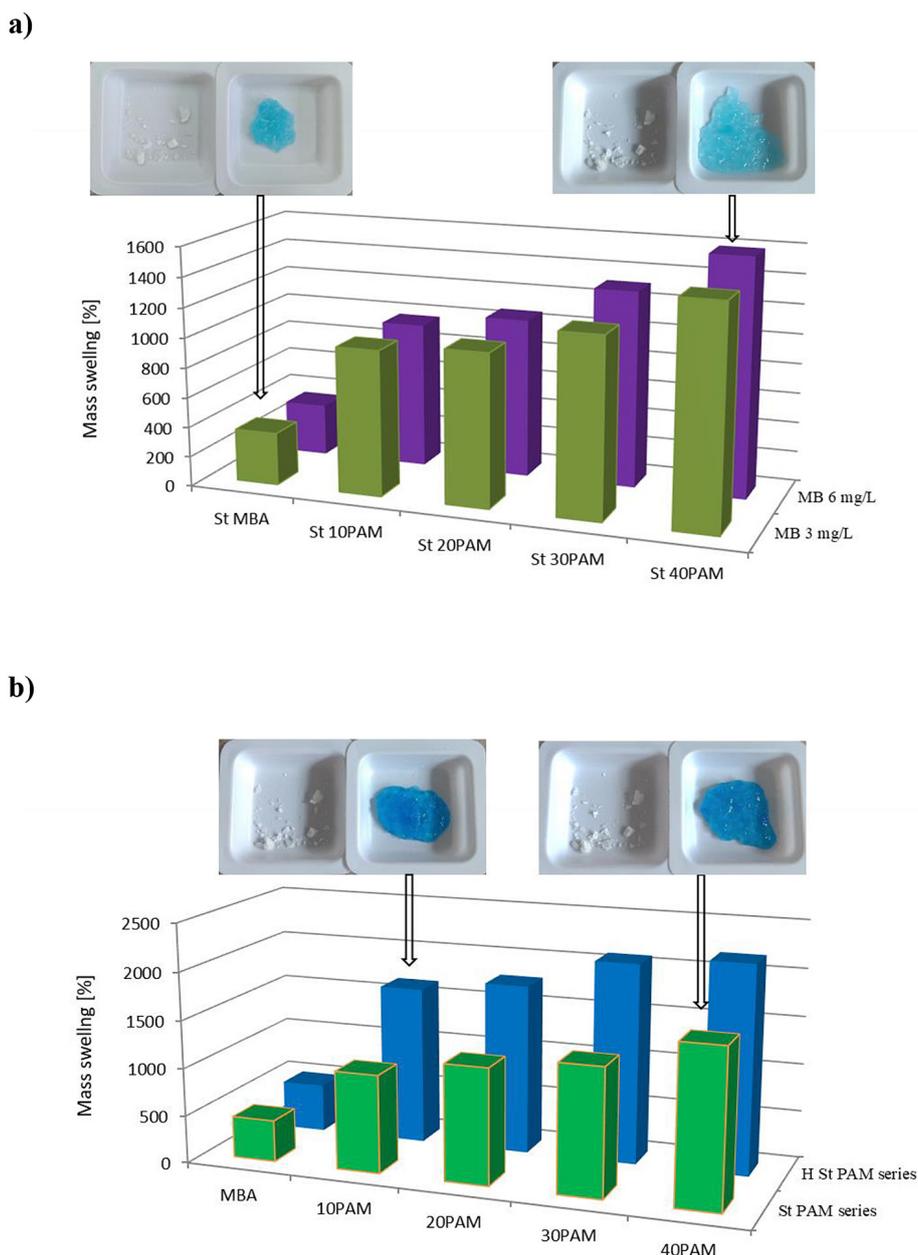
35.5% for H St 40PAM). The conversion of polyacrylamide starch copolymers to their hydrolyzed counterparts resulted in significant improvement in MB removal from the solution because the PAM side chains were extended due to the repulsion between the carboxylate groups [36]. This in turn results in easier penetration of solutions into the interior of the sorbents.

Adsorption efficiency of MBA after 2, 24 and 48h for starch SAPs with different amount of PAM from 10 to 40 wt.% hydrolyzed and non-hydrolyzed is presented in Figure 9. The results showed that the MB sorption efficiency for the basic series from St 10PAM to St 40PAM (Figure

9a) stabilizes with time. The entire series of copolymers reaches similar adsorption efficiency after 24 and 48 h, about 35 and 42 mg MB/g of sorbent, respectively. However, for the series of hydrolyzed copolymers from H ST 10PAM to H St 40PAM, the adsorption efficiency is mainly influenced by the copolymer structure and the contact time of the solution with the sorbent. The adsorption capacity of the materials increases with the increase of the amount of amide and carboxyl groups in the sorbent and time. The sorption properties are improved for hydrolyzed materials due to the appearance of additional active sites - negative groups (-COO<sup>-</sup>) attractive for the attachment



**Figure 9.** Adsorption efficiency of MBA after 2, 24 and 48h for starch SAPs with different amount of PAM from 10 to 40 wt.% a) non-hydrolyzed, b) hydrolyzed



**Figure 10.** Mass swelling of cross-linked starch (St MBA) and St-g-PAM with 10 to 40 wt.% of PAM: a) for MB initial concentration 3 mg/L and 6 mg/L, b) for St PAM and H St PAM series in MB initial concentration 10 mg/L; and selected photos of materials before and after MB sorption

of a cationic dye. It can be assumed that the sorption process stabilizes up to 24 h (the results after 24h and 48h are slightly different). The best results were obtained for hydrolyzed starch SAP with the highest PAM content (after 2h – 54 mg MB/g of sorbent, and after 24h and 48h – 86 and 88 mg MB/g of sorbent, respectively) – Figure 9b.

The swelling properties of the synthesized materials strongly depend on the SAP structure, while they are less dependent on the initial dye concentration (Figure 10). All swollen SAPs were homogeneous gels with a slight blue color from MB (see

photos Figure 10). St MBA showed about 360–400% mass swelling independently of the initial MB solution concentration. The swelling capacity of starch materials increases with increasing PAM content in the absorbent (970% and 1600% for St 10PAM and St 40PAM, respectively) – Figure 10a. The swelling capacity results match very well the results from the adsorption tests. The best swelling results were obtained for the hydrolyzed series and the highest mass swelling was shown by the H St 40PAM sorbent (7 times bigger than for St MBA, 2100%) – Figure 10b.

## CONCLUSIONS

Starch superabsorbent were synthesized using St and different amounts of PAM. The SAPs were synthesized by radical polymerization with ammonium persulfate as initiator. The N,N'-methylenebisacrylamide (MBA) was a cross-linking agent. The basic series consisted of starch-g-polyacrylamide materials, which were additionally hydrolyzed by NaOH solution. The FTIR and XRD spectra, and thermal analysis (DSC and TG) confirmed the successful grafting of PAM onto the starch backbone and alkaline partial hydrolysis of PAM (formation of carboxyl groups from amide groups). The sorption of MB from aqueous solutions was investigated depending on the initial concentration of the MB solution, the contact time of the sorbent with the solution, the amount of PAM grafted onto starch and the structure of the sorbent (hydrolyzed or non-hydrolyzed material). The results showed that increasing the amount of polyacrylamide in the starch sorbent and its hydrolysis, and contact time significantly improved the mass swelling and sorption efficiency of methylene blue from an aqueous solution. A satisfactory adsorption efficiency of 42 mg MB/g sorbent for non-hydrolyzed material was achieved for starch copolymer with 40 wt.% of AM after 2 days (St 40PAM). The best MB sorption result was obtained for the hydrolyzed material with the highest PAM content (H St 40PAM): swelling mass – 2100% and adsorption efficiency – 88 mg MB/g of sorbent. Very satisfactory sorption properties result from the hydrophilicity of polyacrylamide. In addition, sorption properties are additionally enhanced by the attraction of anionic carboxyl groups and cationic dye in hydrolyzed polyacrylamide starch copolymer.

## Acknowledgements

The author would like to thank Ms. Kamila Apanowicz for taking photos of the sorbents.

## REFERENCES

1. Mu Z., Liu D., Lv J., Chai D-F., Bai L., Zhang Z., Dong G., Li J., Zhang W. Insight into the highly efficient adsorption towards cationic methylene blue dye with a superabsorbent polymer modified by esterified starch. *J. Environ. Chem. Eng.* 2022, **10**(5), 108425. <https://doi.org/10.1016/j.jece.2022.108425>

2. Arayaphan J., Maijan P., Boonsuk P., Chantarak S. Synthesis of photodegradable cassava starch-based double network hydrogel with high mechanical stability for effective removal of methylene blue. *Int. J. Biol. Macromol.* 2021, **168**, 875–886. <https://doi.org/10.1016/j.ijbiomac.2020.11.166>
3. Mujtaba G., Ullah A., Khattak D., Shah M.U.H., Daud M., Ahmad S., Hai A., Ahmed F., Alshahrani T., Banat F. Simultaneous adsorption of methylene blue and amoxicillin by starch-impregnated MgAl layered double hydroxide: Parametric optimization, isothermal studies and thermo-kinetic analysis. *Environ. Res.* 2023, **235**, 116610. <https://doi.org/10.1016/j.envres.2023.116610>
4. Taweekarn T., Wongniramaikul W., Boonkanon C., Phanrit C., Sriprom W., Limsakul W., Towanlong W., Phawachalotorn C., Choodum A. Starch biocryogel for removal of methylene blue by batch adsorption. 2022, **14**(24), 5543. <https://doi.org/10.3390/polym14245543>
5. Khan I., Saeed K., Zekker I., Zhang B., Hendi A.H., Ahmad A., Ahmad S., Zada N., Ahmad H., Shah L.A., Shah T., Khan I. Review on methylene blue: its properties, uses, toxicity and photodegradation. *Water* 2022, **14**(2), 242. <https://doi.org/10.3390/w14020242>
6. Rosal R., Rodríguez A., Perdigón-Melón J.A., Petre A., García-Calvo E., Gómez M.J., Agüera A., Fernández-Alba A.R. Occurrence of emerging pollutants in urban wastewater and their removal through biological treatment followed by ozonation. *Water Res.* 2010, **44**(2), 578–588. <https://doi.org/10.1016/j.watres.2009.07.004>
7. Crini G., Lichtfouse E., Wilson L.D., Morin-Crini N. Conventional and non-conventional adsorbents for wastewater treatment. *Environ. Chem. Letters* 2019, **17**, 195–213. <https://doi.org/10.1007/s10311-018-0786-8>
8. Schmidt B. and Zubala A. Rice starch as a polymer sorbent of iron cations. *Polimery/Polymers* 2023, **68**(9), 473 – 479. <https://doi.org/10.14314/polimery.2023.9.3>
9. Shah N., Mewada R.K., Mehta T. Crosslinking of starch and its effect on viscosity behaviour. *Rev. Chem. Eng.* 2016, **32**, 381–481. <https://doi.org/10.1515/revce-2015-0047>
10. Qiao D., Liu H., Yu L., Bao X., Simon G.P., Petinakis E., Chen L. Preparation and characterization of slow-release fertilizer encapsulated by starch-based superabsorbent polymer. *Carbohydr. Polym.* 2016, **147**, 146–154. <https://doi.org/10.1016/j.carbpol.2016.04.010>
11. Ashogbon A.O., Akintayo E.T. Recent trend in the physical and chemical modification of starches from different botanical sources: A review. *Starch Stärke* 2014, **66**, 41–57. <https://doi.org/10.1002/>

- [star.201300106](https://doi.org/10.1002/app.23956)
12. Zhang S., Chen H., Liu S., Guo J. Superabsorbent polymer with high swelling ratio, and temperature-sensitive and magnetic properties employed as an efficient dewatering medium of fine coal. *Energy Fuels* 2017, 31, 1825–1831. <https://doi.org/10.1021/acs.energyfuels.6b03083>
  13. Xiao X., Yu L., Xie F., Bao X., Liu H., Ji Z., Chen L., Xie F. One-step method to prepare starch-based superabsorbent polymer for slow release of fertilizer. *Chem. Eng. J.* 2017, 309, 607–616. <https://doi.org/10.1016/j.ccej.2016.10.101>
  14. He Y., Tang H., Chen Y., Zhang S. Facile Strategy to Construct Metal-Organic Coordination Thermoplastic Starch with High Hydrophobicity, Glass-Transition Temperature, and Improved Shape Recovery. *ACS Sustain. Chem. Eng.* 2020, 8, 8655–8663. <https://doi.org/10.1021/acssuschemeng.0c01579>
  15. Soltovski de Oliveira C.S., Andrade M.M.P., Colman T.A.D., Da Costa F.J.O.G., Schnitzler E. Thermal, structural and rheological behaviour of native and modified waxy corn starch with hydrochloric acid at different temperatures. *J. Therm. Anal. Calorim.* 2014, 115, 13–18. <https://doi.org/10.1007/s10973-013-3307-9>
  16. Szychaj T., Schmidt B., Ulfig K., Markowska-Szczupak A. Starch-grafted-N-vinylformamide copolymers manufactured by reactive extrusion: Synthesis and characterization. *Polimery/Polymers* 2012, 57, 95–100. <https://polimery.ichp.vot.pl/index.php/p/article/view/809/896>
  17. Haseeb M.T., Hussain M.A., Yuk S.H., Bashir S., Nauman M. Polysaccharides based superabsorbent hydrogel from Linseed: Dynamic swelling, stimuli responsive on–off switching and drug release. *Carbohydr. Polym.* 2016, 136, 750–756. <https://doi.org/10.1016/j.carbpol.2015.09.092>
  18. Ibrahim B., Fakhre N. Crown ether modification of starch for adsorption of heavy metals from synthetic wastewater. *Int. J. Biol. Macromol.* 2019, 123, 70–80. <https://doi.org/10.1016/j.ijbiomac.2018.11.058>
  19. Lapointe M., Barbeau B. Substituting polyacrylamide with an activated starch polymer during ballasted flocculation. *J. Water Process. Eng.* 2019, 28, 129–134. <https://doi.org/10.1016/j.jwpe.2019.01.011>
  20. Schmidt B., Kowalczyk K., Zielińska B. Synthesis and characterization of novel hybrid flocculants based on potato starch copolymers with hollow carbon spheres. *Materials* 2021, 14(6), 1498. <https://doi.org/10.3390/ma14061498>
  21. Jiraprasertkul W., Nuisin R., Jinsart W., Kiatkamjornwong S. Synthesis and characterization of cassava starch graft poly(acrylic acid) and poly[(acrylic acid)-co-acrylamide] and polymer flocculants for wastewater treatment. *J. Appl. Polym. Sci.* 2006, 102, 2915–2928. <https://doi.org/10.1002/app.23956>
  22. Khoo P.S., Ilyas R. A., Uda M. N. A., Hassan S.A., Nordin A. H., Norfarhana A. S., Ab Hamid N. H., Rani M. S. A., Abrial H., Norrrahim M. N. F., Knight V. F., Lee C.L., Ayu Rafiqah S. Starch-Based Polymer Materials as Advanced Adsorbents for Sustainable Water Treatment: Current Status, Challenges, and Future Perspectives. *Polymers* 2023, 15, 3114. <https://doi.org/10.3390/polym15143114>
  23. Abd El-Ghany N.A., Abu Elella M.H., Abdallah H.M., Mostafa M.S., Samy M. Recent Advances in Various Starch Formulation for Wastewater Purification via Adsorption Technique: A Review. *J. Polym. Environ.* 2023, 31, 2792–2825. <https://doi.org/10.1007/s10924-023-02798-x>
  24. Zamani-Babgohari F., Irannejad A., Pour M.K., Khayati G.R. Synthesis of carboxymethyl starch co (polyacrylamide/ polyacrylic acid) hydrogel for removing methylene blue dye from aqueous solution. *Intern. J. Biol. Macromol.* 2024, 269(1), 132053. <https://doi.org/10.1016/j.ijbiomac.2024.132053>
  25. Ahmed E.M. Hydrogel: preparation, characterization, and applications: a review. *J. Adv. Res.* 2015, 6(2), 105–121. <https://doi.org/10.1016/j.jare.2013.07.006>
  26. Keshava Murthy P.S., Murali Mohan Y., Sreeramulu J., Mohana Raju K. Semi-IPNs of starch and poly(acrylamide-co-sodium methacrylate): Preparation, swelling and diffusion characteristics evaluation. *React. Funct. Polym.* 2006, 66(12), 1482–1493. <https://doi.org/10.1016/j.reactfunctpolym.2006.04.010> [Get rights and content](#)
  27. Matovanni M.P.N., Distantina S., Kaavessina M. Synthesis of cassava starch-grafted polyacrylamide hydrogel by microwave-assisted method for polymer flooding. *Indones. J. Chem.*, 2022, 22(3), 791 – 804. <https://doi.org/10.22146/ijc.71343>
  28. Zhang J., Li A., Wang A. Study on superabsorbent composite. VI. Preparation, characterization and swelling behaviors of starch phosphate-graft-acrylamide/attapulgit superabsorbent composite. *Carbohydr. Polym.* 2006, 65, 150–158. <https://doi.org/10.1016/j.carbpol.2005.12.035>
  29. Bao, X., Yu, L., Shen, S., Simon, G.P., Liu, H., Chen, L. How rheological behaviors of concentrated starch affect graft copolymerization of acrylamide and resultant hydrogel. *Carbohydr. Polym.* 2019, 219, 395–404. <https://doi.org/10.1016/j.carbpol.2019.05.034> [Get rights and content](#)
  30. Schmidt B., Rokicka J., Janik J., Wilpiszewska K. Preparation and characterization of potato starch copolymers with a high natural polymer content for the removal of Cu(II) and Fe(III) from Solutions. *Polymers* 2020, 12(11), 2562. <https://doi.org/10.3390/polym12112562>

31. Qiao D., Tu W., Wang Z., Yu L., Zhang B., Bao X., Jiang F., Lin Q. Influence of crosslinker amount on the microstructure and properties of starch-based superabsorbent polymers by one-step preparation at high starch concentration. *Int. J. Biol. Macromol.* 2019, 129, 679–685. [10.1016/j.ijbiomac.2019.02.019](https://doi.org/10.1016/j.ijbiomac.2019.02.019)
32. Schmidt, B. Effect of crosslinking agent on potato starch grafted acrylamide copolymers and their sorption properties for water, Fe<sup>3+</sup> and Cu<sup>2+</sup> cations. *Polimery/Polymers* 2018, 63, 347–352. <https://doi.org/10.14314/polimery.2018.5.3>
33. Zhou Y., Meng S., Chen D., Zhu X., Yuan H. Structure characterization and hypoglycemic effects of dual modified resistant starch from indica rice starch. *Carbohydr. Polym.* 2014, 103, 81–86. <https://doi.org/10.1016/j.carbpol.2013.12.020>
34. Zdanowicz, M., Schmidt, B., Szychaj, T. Starch graft copolymers as superabsorbents obtained via reactive extrusion processing. *Pol. J. Chem. Technol.* 2010, 12, 14–17. <https://doi.org/10.2478/v10026-010-0012-3>.
35. Hoover, R., Hughes, T., Chung, H., Liu, Q. Composition, molecular structure, properties, and modification of pulse starches: A review. *Food Res. Int.* 2010, 43, 399–413. <https://doi.org/10.1016/j.foodres.2009.09.001>
36. Tungala K., Maurya A., Adhikary P., Sonker E., Kerketta A., Karmakar N.C., Krishnamoorthi S. Flocculation characteristic of tapioca starch grafted polyacrylamide in kaolin and opencast coal mines dust suspensions and methylene blue dye removal. *Res. J. Life Sci. Bioinform. Pharm. Chem. Sci.* 2017, 2(5), 138–155. <https://doi.org/10.26479/2017.0205.13>
37. Hu J., Tian T., Xiao Z. Preparation of cross-linked porous starch and its adsorption for chromium (VI) in tannery wastewater. *Polym. Adv. Technol.* 2015, 26, 1259–1266. <https://doi.org/10.1002/pat.3561>
38. Qiao D., Yu L., Bao X., Zhang B., Jiang F. Understanding the microstructure and absorption rate of starch-based superabsorbent polymers prepared under high starch concentration. *Carbohydr. Polym.* 2017, 175, 141–148. <https://doi.org/10.1016/j.carbpol.2017.07.071> Get rights and content.
39. Malatji N., Makhado E., Modibane K.D., Ramohlola K.E., Maponya T.C., Monama G.R., Hato M.J. Removal of methylene blue from wastewater using hydrogel nanocomposites: A review. *Nanomater. Nanotechnol.* 2021, 11, 1–27. <https://doi.org/10.1177/18479804211039425>
40. Junlapong K., Maijan P., Chaibundit C., Chantarak S. Effective adsorption of methylene blue by biodegradable superabsorbent cassava starch-based hydrogel. *Internat. J. Biol. Macromol.* 2020, 158, 258–264. <https://doi.org/10.1016/j.ijbiomac.2020.04.247>