Rice starch as a polymer sorbent of iron cations*)

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Abstract: Native, gelatinized and cross-linked rice starch was used to prepare "green sorbents". FTIR, XRD, SEM, DSC and TGA methods were used to evaluate the properties of the obtained materials. The influence of the type of starch, sorbent dose and contact time on the sorption efficiency was examined. The swelling properties, the degree of solution purification and the efficiency of Fe(III) ion removal were determined. The sorption properties of the materials strongly depended on the type of starch and the conditions of their use.

Keywords: starch, sorbents, modification, sorption properties.

Skrobia ryżowa jako polimerowy sorbent kationów żelaza

Streszczenie: Skrobię ryżową natywną, zżelowaną i usieciowaną użyto do otrzymywania „zielonych sorbentów". Do oceny właściwości otrzymanych materiałów zastosowano metody FTIR, XRD, SEM, DSC i TGA. Zbadano wpływ rodzaju skrobi, dawki sorbentów i czasu kontaktu na efektywność sorpcji. Oznaczono właściwości pęczniejące, stopień oczyszczania roztworu i skuteczność usuwania jonów Fe(III). Właściwości sorpcyjne materiałów silnie zależały od rodzaju skrobi i warunków ich stosowania.

Słowa kluczowe: skrobia, sorbenty skrobiowe, modyfikacja skrobi, właściwości sorpcyjne.

Polymer sorbents are three-dimensional polymer networks, most often cross-linked hydrophilic polymers, capable of absorbing and retaining significant amounts of water, dyes, or ions [1–3]. Polymer sorbents are widely used, e.g., in hygiene products [4, 5], slow-release fertilizers [6, 7] and drug delivery systems [8]. Over the last 30 years, thousands of publications on superabsorbents have appeared [2], but the authors focused primarily on synthetic polymers and copolymers because of their better price-performance ratio. However, the published results regarding starch sorbents are based on modified starch from corn and potatoes due to increased efficiency of solution purification [9–11], but each modification of the raw material requires additional energy, materials, human resources and absorbs time.

Starch is a common and widely available natural polymer, which is a reserve material of plants, found in their seeds, stems, roots and fruits. It is obtained from corn, wheat, rice, potatoes, and tapioca. In addition to food applications, it is widely used in other industries, including chemical, paper or mining [12, 13]. Due to easy modification and natural origin, starch is still of interest to scientists as a substrate for a new material, e.g., sorbents [14–15]. The genotype of starch determines its physicochemical properties such as grain size, shape, association (single or clusters of grains), structure, gelatinization temperature [16, 17], and thus the tendency to modification, e.g., cross-linking [18, 19]. Starch can be modified physically, enzymatically, and chemically, continuously by reactive extrusion or periodically in the reactor [12, 20, 21].

In line with developing pro-ecological trend, solutions based on environmentally friendly materials, such as natural polymers, are constantly in request. Starch constitutes about 80% of the rice composition. Rice storage is an intermediate stage between its harvest and consumption. However, during rice storage, many physicochemical changes can occur, e.g., an increase in hardness. Moreover, due to improper storage of rice and the clumping of rice grains into agglomerates, its quality is much worse and, consequently, it becomes inedible [22, 23]. Currently, inedible rice is being reprocessed and the use of "waste" rice as a source of starch (being a substrate for "green" sorbents) creates new opportunities that are beneficial both economically and environmentally. Additionally, because starch can complex cations of various metals [24, 25] and the limited amount of information about rice starch absorbents, the authors of this publication present results regarding three forms of rice starch sorbents.

The aim was to obtain rice starch sorbents and to experimentally determine their ability to be used as sorbents of Fe(III) cations from aqueous solution. Iron

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cations were selected due to their common occurrence in water causing unwanted coloration. Moreover, the removal of Fe(III) cations from solutions by starch materials is often considered in the context of flocculation [26, 27], and very rarely sorption [3]. Therefore, in this work, the sorption and mass swelling properties of the native rice starch (RSN), the gelatinized starch (RSG) and the cross-linked starch (RSC) were investigated depending on the dose of sorbent and the contact time of the sample with the solution. The sorbents were obtained through easy physicochemical modifications (gelatinization or cross-linking). The starch sorbents ware characterized using Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermal analysis (TGA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Differences in the sorption properties of starch materials were explained by the diversity of their structure and morphology.

EXPERIMENTAL PART

Materials

Rise starch (RSN), super standard quality (about. 99%), moisture about 15% was purchased from Sigma-Aldrich. Gelatinized rise starch (RSG) was obtained by heating starch in distilled water (4,56 g RSN in 150 cm^3, 80°C, 30 min.) and then precipitated in acetone and dried at 80°C. Cross-linked starch (RSC) was received by adding N,N′-methylenebisacrylamide (MBA, 99%, Merck, Germany, 0.5 wt%) to suspension of RSG (stirred under nitrogen, 1.5 h, 80°C) as in the reference [3]. Aqueous Fe(III) cations solution with a concentration of 30 mg Fe^{3+}/L was prepared from hydrated sulfate (analytical grade, POCH Gliwice, Poland) and acetone (analytical reagent grade) used to precipitate sorbents was purchased from Chempur, Poland. All materials were used without further purification.

Methods

FTIR spectra of dried powdered samples of starch sorbents were obtained using a Nexus FTIR spectrometer (Thermo Nicolet Corp., USA) with a Golden Gate accessory (ATR) and the OMNIC computer program. The thermal properties were determined by thermogravimetric analysis (TGA) using a Q5000 thermobalance (TA Instruments Inc., USA), at a heating rate of 10°C/min, from 30 to 900°C and differential scanning calorimetry (DSC) by Q100 DSC apparatus (TA Instruments Inc., USA) at a heating rate of 10°C/min, from 0 to 250°C. The surface morphology was examined by scanning electron microscopy (SEM, SU 8020, Hitachi, Japan) at an accelerating voltage of 5 kV and a current of 10 μA. Samples were sprayed with a 5 nm layer of chromium to avoid electrical charging. Crystallinity was determined by X-ray diffraction (XRD) with Empyrean X-ray diffractometer (Malvern Panalytical, Malvern, UK), employing CuKα radiation, λ = 1.544 Å, 7–90°, 0.01°/s. The sorption tests were carried out on mechanically powdered materials with particles diameter of less than 0.3 mm. The initial concentrations of iron(III) cations in solution were 30 mg Fe^{3+}/L and sorbents doses were: 5, 10, 25 and 50 mg in 50 mL. Removal of Fe(III) ions was controlled spectrophotometrically by changes in the absorbance of colored solutions in time (UV-9000 apparatus, BioSens, wavelengths 480 nm, up to 120 min) and calculated from a calibration curve with the coefficient R^2=0.997. The determination of mass swelling for starch sorbents was based on the references [3]. The swelling measurements were performed at room temperature after 2, 24 and 48 hours for all doses of sorbents used. After the designated time, the sorption material was separated from the solution and weighed. The results were averaged from three measurements for the same material.

RESULTS AND DISCUSSION

Rice starch sorbents were characterized by FTIR to confirm starch cross-linking (Fig. 1). A typical FTIR spectrum of RSN shows a wide band in the wavelength range 3650–3000 cm^{-1} (the presence of OH groups – stretching vibrations), at 2900 cm^{-1} (stretching vibrations of the C-H and symmetrical CH_2 groups), at 1460 and 1380 cm^{-1} (O–H in-plane bending vibrations) and sharp three peaks close together at 1160, 1080 and 1015 cm^{-1} (C-O-C stretching vibrations) [28, 29]. Changes in the RSG spectrum at wavelengths at 2900 cm^{-1} and 1640 cm^{-1} can be attributed to water absorption in the amorphous region of starch [30]. The new adsorption bands in RSC spectra at 1680 cm^{-1} and 1640 cm^{-1} (the stretching vibration of –C=O and –N–H bending vibrations representative for the MBA) proved the cross-linking of starch [31].

The appearance of the RSN grains and the surface morphology of the remaining sorbents are shown in SEM images (Fig. 2). Native rice starch occurs in the form of round, irregular granules ranging from 3 to 8 μm in size, forming small clusters (Fig. 2a). On the other hand, the modified starches are non-uniform lumps with a rough and irregular surface (Fig. 2b and 2c). However, no morphological differences were observed between RSG and RSC.

The recorded XRD patterns for all tested forms of rice starch also confirmed the modification of the raw material (Fig.3). The RSN gave a strong diffraction peak at 15°, 17.5°, 18° and 20° 2θ and an additional peak at 24° 2θ, which is the characteristic scattering features of a semi-crystalline polymer [32]. The double helices of amylopectin form a specific crystalline structure, while the branches of the amylopectin chains and the single helices of amylose form an amorphous structure [17]. Gelatinization and cross-linking destroy the semi-crystalline structure of starch. The XRD spectra of the RSG and RSC samples show one large diffuse peak in the spectrum and confirm the almost amorphous nature of the materials.

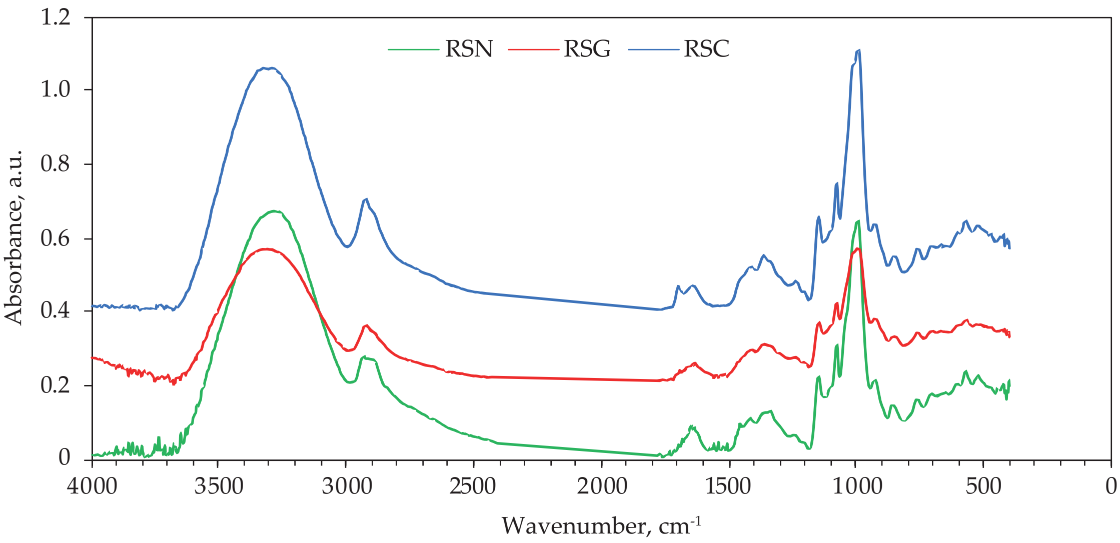

Fig. 1. FTIR spectra of RSN, RSG and RSC

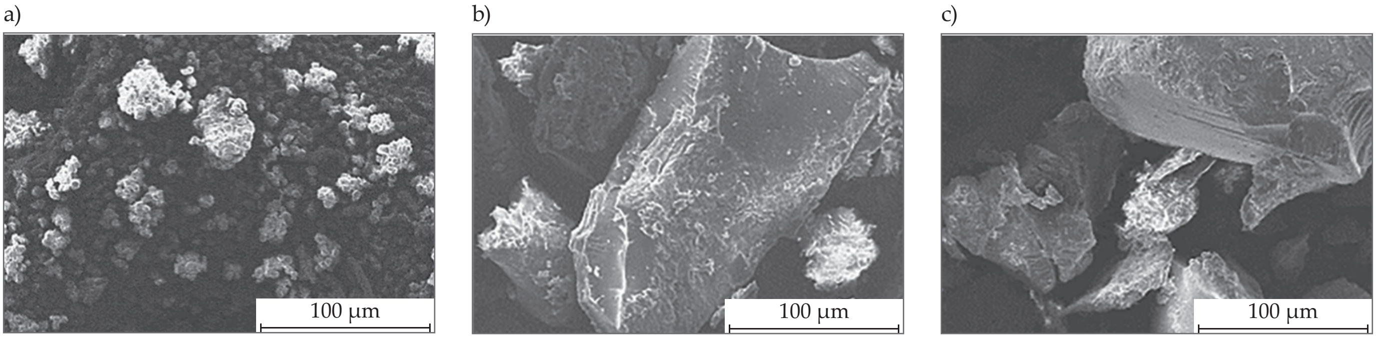

Fig. 2. SEM images of starch sorbents: a) RSN, b) RSG, c) RSC

Thermal properties (Fig. 4 and 5) also validated the diversity of the obtained starch materials. The thermogravimetric curves shown in Fig. 4 have a similar shape with a slight shift towards to higher temperature (by 30°C) for modified starches in the last phase of decomposition. The RSN loses water quickly up to 100°C, thus reducing mass by approximately 9%. Modified starches lose water more slowly than RSN at temperatures of 30– 270°C and lose about 7.5% of their mass during dehydration (the first stage of starch sorbents decomposition) [3, 7]. The second stage at 270–330°C is the degradation of the starch backbone, which corresponds to the loss of hydroxyl groups and depolymerization of carbon chains (70% weight loss for all samples). Last stage above 330°C is due to carbonization of starch.

The DSC heat flow thermographs of starch sorbents are shown in the Fig.5. For raw starch, the maximum of the endothermic peak is at 152°C, which is consistent with a study by Xu *et al.* [33]. The melting points of RSG and RSC are 176°C and 174°C, respectively, that can be explained by starch cross-linking or reduction of free water (samples were dried at 80°C for 24 h before DSC testing) [34].

The sorption study of Fe(III) from the aqueous solutions (30 mg Fe(III)/L) in dependence of absorbance as the function of time for different sorbents doses was graphically illustrated in Figure 6 and 7. Additionally, Table 1 shows the iron(III) removal efficiency dependent on the type, dose of materials and contact time of the liquid and solid phases. The calculations of amount of iron cations removed were made indirectly by determining a calibration curve for solutions with Fe(III) concentrations from 1 to 30 mg/L. The purification of solutions was investigated at various doses of sorbents (5, 10, 25, 50 and 100 mg) within 120 min (Fig. 6), while mass swelling tests were carried out at time intervals of 2, 24 and 48 h (Fig. 7).

Figure 6 illustrates purification of the cation solution by RSN, RSG and RSC sorbents. Fig. 6a has a different absorbance scale than the other graphs in Fig. 6 to precisely show the turbidity of the solutions in the first minutes of the tests. Natural rice starch shows sorption properties and the absorbance after 120 min of the test was in the range of 0.09 - 0.16. The suspension with the highest dose of RSN was the most turbid (absorbance 1.195 at time 0 min, 0.63 at 5 min, and 0.16 at 120 min), which results from the type of starch - light, slowly sedimenting, fine-grained. The higher dose of RSN, the greater absorbance of the solution. This means that the purification of solutions requires a longer time for RSN compared to modified sorbents, and on the other hand, a similar effect is achieved at a lower dose.

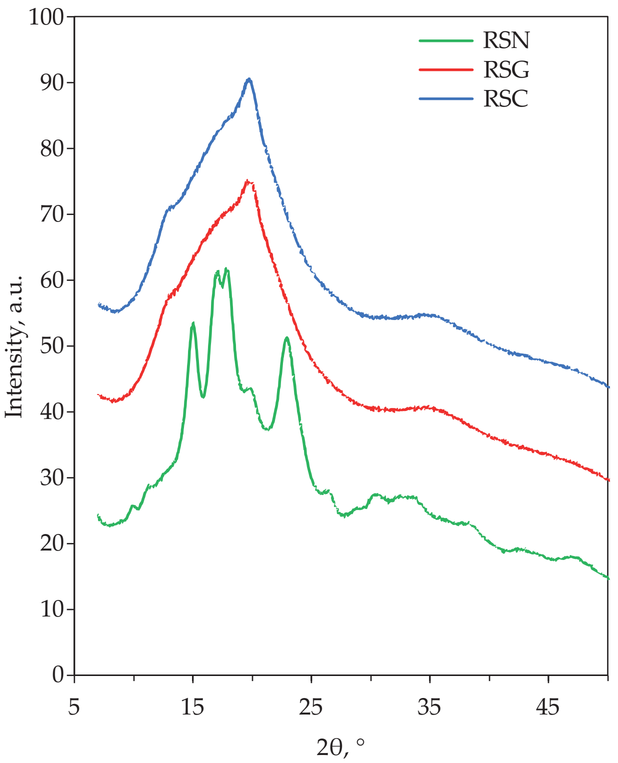

Fig. 3. XRD patterns of RSN, RSG and RSC

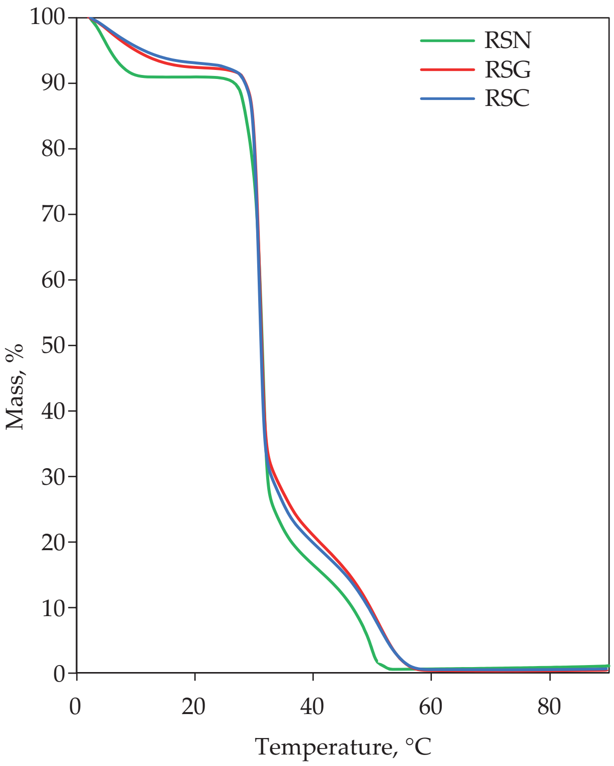

Fig. 4. The thermogravimetric curves of RSN, RSG and RSC

Modified starches (Fig. 6b and 6c) show comparable properties in purifying solutions from Fe(III) and the sorption results were satisfactory in both cases. Finally, the reduction in turbidity was in the absorbance range 0.07–0.10 for RSG and 0.10–0.11 for RSC. However, for RSC (Fig. 6c), changes in the absorbance of solutions did not depend only on the sorbent dose (they also depend on the contact time), while for RSG – the higher sorbent dose, the clearer solution.

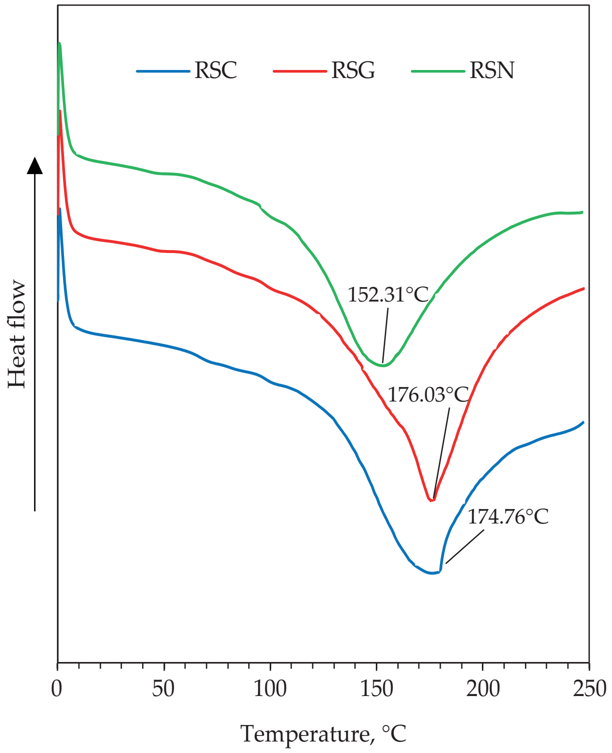

Fig. 5. DSC thermograms of RSN, RSG and RSC

The removal of Fe(III) ions from solutions within 10, 30, and 100 min for all doses and sorbents used is summarized in Table 1. Iron removal efficiency increases and stabilizes over time. After the first 10 minutes of the tests, only modified starches removed 7–8 mg of Fe(III) from the solution, and the best results were obtained for a dose of 25 mg for both RSG and RSC, while RSN needs time to break down grain agglomerates and swell. After 30 min, the sorption of Fe(III) cations increases to 6–7 mg for RSN and to 12 mg of Fe(III) for RSG. Even a slight modification (gelatinization) improves the sorption properties of the natural polymer by 43%. The iron removal efficiency after 30 min is the highest for RSC (13 mg Fe^{3+}) and it is related to the saturation of the cross-linked sorbent. This is indicated by the lack of correlation between the dose and cation sorption and the achievement of almost identical results after 100 min. The iron removal efficiency after 100 min for RSN and RSG is comparable (15 and 16 mg Fe^{3+} for 100 mg of sorbent, respectively).

There are several fundamental factors that determine the swelling properties of sorbents e.g., the degree of cross-linking, the number of polar groups/ions present, temperature, drying techniques and contact time of two phases. Figure 7 shows changes in mass swelling (the amount of sorbed liquids in relation to the initial sample mass

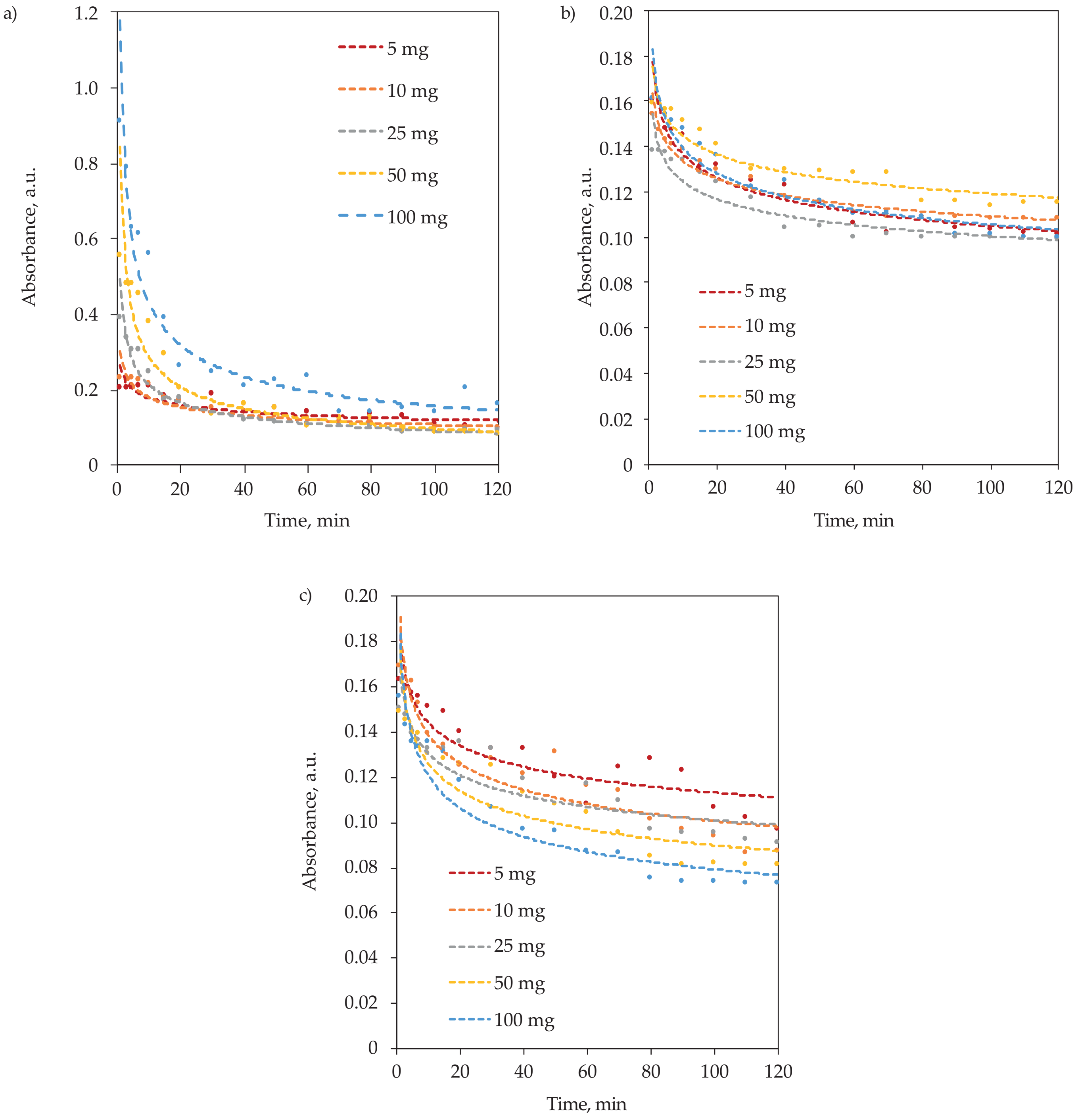

Fig. 6. Absorbance of the Fe(III) in aqueous solution as a function of time for different doses of sorbent: a) RSN, b) RSG, c) RSC

mg/mg) [3] for all sorbents after contact times of 2, 24, and 48 h. The mass swelling of RSN (Fig. 7a) was the smallest of the tested sorbents. The RSN absorbs solution in the range of 4.6–7.9 times its initial sample mass. The disintegration of non-cross-linked starch grains during swelling in aqueous solutions is noticeable by obtaining lower mass swelling values with an increase in the sorbent dose. In the case of RSN, the material disintegrated completely after 24 hours (Fig. 7a). The RSG achieves excellent swelling indicators in the range 8.5–13.5 up to 24 hours, while after 48 hours all results are almost identical (1.5) but not very satisfactory (Fig. 7b). Figure 7c shows the significant effect of materials cross-linking on swelling properties. The RSC demonstrates a stable mass swelling capacity, which increases slightly over time and, most importantly, maintains its satisfactory swelling after 48 hours.

CONCLUSIONS

A simple procedure to prepare various rice starches (gelatinization and cross-linking with a small amount of MBA) ware applied to obtain "green" sorbents from

Table 1. The Fe(III) removal efficiency depending on material type, dose of sorbents and contact time

Time, min	10					30					100				
Sorbents dose, mg	5	10	25	50	100	5	10	25	50	100	5	10	25	50	100
	Iron removal efficiency, mg Fe^{3+}														
RSN	0	0	0	0	0	2	5	6	7	7	12	13	14	15	15
RSG	4	6	8	8	7	8	8	8	9	12	12	14	14	16	16
RSC	5	6	7	4	5	13	12	13	13	13	13	13	13	13	13

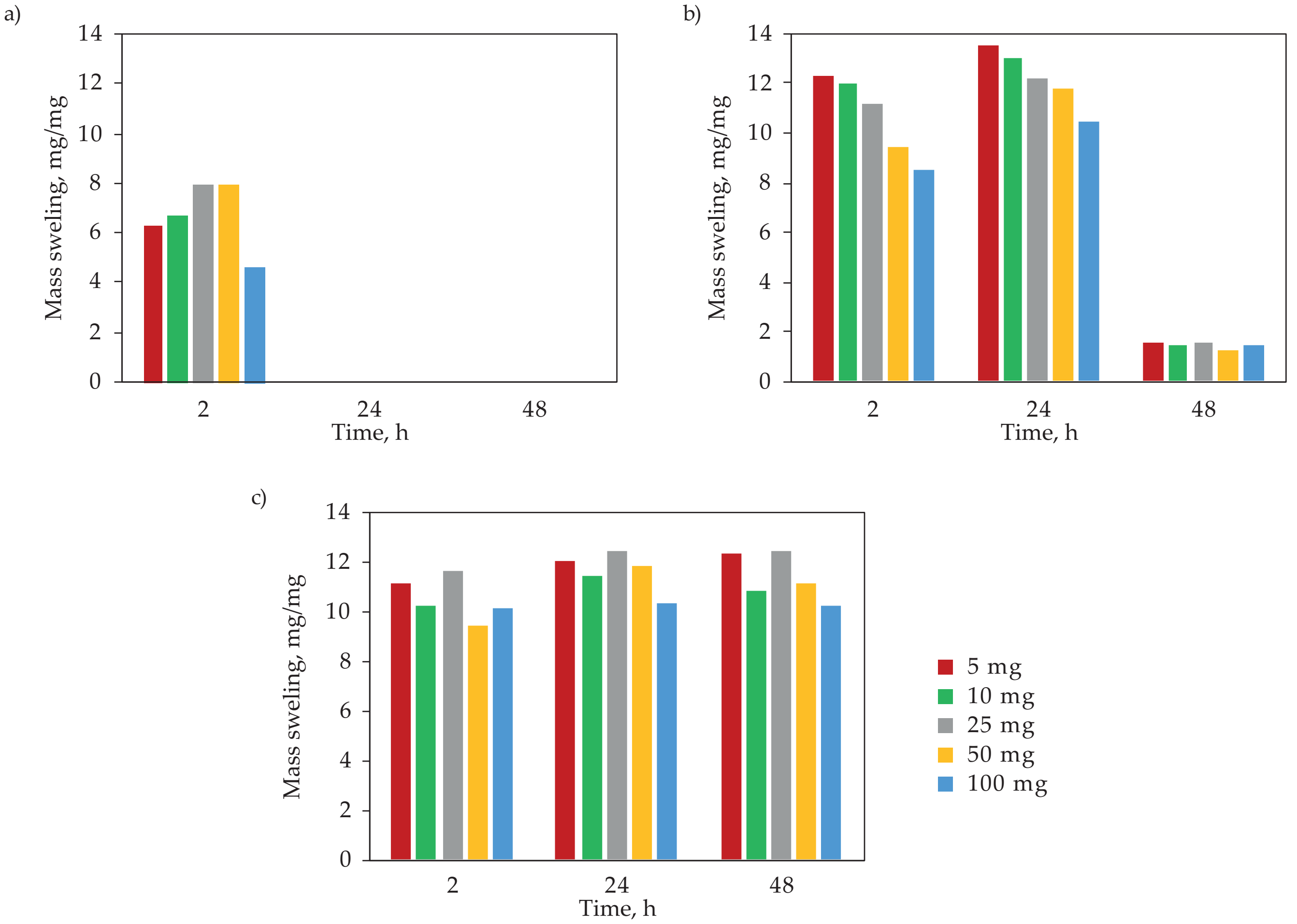

Fig. 7. Mass swelling as a function of time: a) RSN, b) RSG, and c) RSC

natural polymers. The characterization of the received sorption materials indicated their structural diversity. XRD, SEM, TG and DSC methods confirmed that gelatinized starch is characterized by changes in surface morphology, crystallinity and thermal properties compared to natural starch and similarity to cross-linked starch. However, FTIR spectroscopy clearly indicated the same chemical structure of RSG as natural rice starch -RSN. The FTIR method also confirmed the receiving of cross-linked starch- RSC.

In addition to the swelling properties, solution purification and ion sorption were investigated. It was proved that all obtained starch materials show sorption properties. However, their sorption efficiency of Fe(III) cations strongly depends on the form of starch and the conditions of use. Natural rice starch can be used as a super ecological sorbent only in a short time, up to 2 hours, and its sorption capacity reaches a satisfactory level after about 60 minutes. The gelatinized starch shows satisfactory iron ions removal efficiency (16 mg Fe^{3+} for 50 and 100 mg dose), but the recommended time of use is 24 hours, which is sufficient, e.g., to clean home swimming pools. It was confirmed that RSC is the most stable sorbent, and the sorption and swelling properties of this material are dose independent but depend on the number of functional groups and cross-linking. RSC can be used for at least 48 hours without losing its quality, however, the iron removal efficiency for RSC (13 mg Fe^{3+}) is slightly worse than for RSG.

The study confirms the influence of cross-linking on the sorption properties of starch materials. The higher the cross-linking density (RSC), the lower the swelling capacity together with the greater strength of the superabsorbent (48 h). On the other hand, a less dense network makes the material more flexible and absorbs larger amounts of liquids (RSG). Insufficient amount of cross-linking agent or it lack may result in the dissolution or disintegration of the superabsorbent in water/solution (RSN and RSG).

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