Abstract
Global warming has posed a number of challenges for agriculture. The key problem is water retention in soil. Existing irrigation methods are costly and ineffective. To solve this problem, a synthesis of a rare-cross-linked hydrophilic polymer material with the properties of a pectin-based superabsorbent was conducted. Our research showed that the water-adsorbing ability is ensured by the presence of short-sized acrylamide residues, fragments with residues of carboxyl groups and polysaccharide units in the structure. The superabsorbent with pectin as a biodegradable component is able to retain a portion of water of hydration even during prolonged drying. The effect of the pH of the medium on the water absorption capacity and swelling of the superabsorbent “Solid water” was shown. This superabsorbent can be used in different types of soils, as confirmed by the studies conducted in distilled water, as well as in alkaline and acidic media. The polymer is characterised by the highest swelling values in an alkaline medium due to the electrostatic repulsion of dissociated carboxyl groups, formed as a result of the hydrolysis of acrylamide. This makes it suitable for use in leached soils, such as leached black soil (Chernozem) in the Voronezh region. IR spectroscopy showed the presence of the superabsorbent’s functional groups that form supramolecular structures including bound water molecules with no additional coordinate covalent bonds present. Thus, the reactions can be characterised as processes with the elements of system self-organisation.

Keywords: superabsorbent, hydration properties, water absorption, pectin, IR spectra.

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1. Introduction
Abrupt climatic changes of the past few years have led to global warming, which caused the expansion of dry regions and increased the agricultural risk in these areas. Therefore, one of the key objectives of contemporary agriculture is maintaining the required level of moisture and soil fertility for high harvest yields. Irrigation and application of mineral fertilisers, microelements, and microorganisms are the methods used to solve these problems. However, hydro-amelioration methods applied in the areas with insufficient freshwater resources are sophisticated, costly, and inefficient. The application of a large amount of fertilisers leads to irreversible changes in soil pH, the risk of soil salinisation and exhaustion and the pollution of underground water with derivatives of nitric and phosphoric acids, which negatively affects the state of the plants that consume such water [1].

A promising solution of the above-mentioned problems is the use of new composite organic
hydrophilic polymer materials capable of multiple absorption and slow release of the absorbed water into the soil without changing their properties [2]. Such polymers can be used as water reservoirs for maintaining the required level of moisture and various additives in a wide range of temperatures over a period of several years.

Previously, a synthesis of a rare-cross-linked hydrophilic polymer material with the properties of a superabsorbent was conducted with addition of biodegradable fragments to its structure. When used in the soil, these fragments decompose, increasing moisture capacity and saturating the soil with nitrogen required for the normal vegetation of plants [3]. Pectin was used as one of these fragments.

The aim of this work was the development of synthesis of polymer biodegradable composites with the properties of a superabsorbent and the study of hydration properties of the original material “Solid water”.

2. Experimental

The first stage of synthesis was preliminary preparation of the solution of the biodegradable component in a glass reactor at 40 °C and the redox initiator system H₂O₂+Fe₂(SO₄)₃ for the initiation of radical polymerisation. This mixture was vigorously stirred for 30 minutes and then the solution of acrylamide and the crosslinking agent was added to the reactor. The second stage of synthesis involved stirring for 5 hours at the temperature of 40 °C.

The obtained rare-cross-linked superabsorbents with different content of biodegradable components and specific additives were dried in the flow of warm air, and water surplus was removed using acetone or isopropyl alcohol. The dried polymer material was ground and used for tests [3].

Water absorption by the polymer was determined according to the following method. Equal samples (0.2 g) of the superabsorbent were weighed and put into small organza bags. Water can permeate through this fabric, but is practically not absorbed by it. Each bag with a polymer sample was placed in a separate glass with 500 ml of water. Then the glass was tightly closed and sealed, and 24 hours later the bags with the samples were removed from the glasses.

The volume of the remaining water was measured using a measuring cylinder, and the volume of water absorbed by the sample was calculated as the difference between the original and the remaining volume. After that, the calculations were made taking into account the water adsorption of 1 kg of the polymer.

IR spectroscopy of the powder samples fixed by a holder on the sensitive surface of the prism was conducted on the Bruker Vertex 70v vacuum FTIR spectrometer using a “Platina” single-pass ATR adapter.

3. Results and discussion

The specific feature of the structure of the superabsorbent “Solid water” is the result of choosing special monomers for the synthesis and developing the conditions of the synthesis itself. Fig. 1 shows one of the possible schematic structures of the superabsorbent which demonstrates that water-adsorbing ability is secured by the presence of short-sized acrylamide residues, fragments with residues of carboxyl groups and polysaccharide units in the structure. A necessary condition of

Fig. 1. Scheme of the polymer
a considerable amount of water absorbed by a sorbent is mechanical stability of polyelectrolyte chains in the processes of association and reassociation of the solvent molecules.

In this case, one may talk of common properties of polyelectrolyte chains of the superabsorbent and intracellular membranes which are able to ensure smooth transport of water molecules (Fig. 2).

$$\begin{align*}
R-\text{COOH} + H_2O &= R-\text{COO}^{-}H_2O^+ \\
R-\text{COO}^{-}H_2O^+ + nH_2O &= [R-\text{COO}^{-}H_2O^+]_{nH_2O} \\
R-NH-(CH_3)_2-OH^+ + nH_2O &= [R-NH-(CH_3)_2-OH^-]_{nH_2O}^2 \\
\end{align*}$$

**Fig. 2.** General scheme of water absorption by sorbents

The integrity of exceptionally thin structures is maintained in polyelectrolyte chains in the “Solid water”, as for biomembranes, due to polar interactions and variance relationships. There is no data indicating the presence of covalent and coordination bonds between successive molecules of lipids and between adjacent lipid and protein molecules in membranes. A similar effect was observed during the interaction of polyelectrolyte chains in the “Solid water” polymer with amide and –COOH-groups of neighbouring chains. The difference in the considered case is that intracellular membranes are based on phospholipids while the chains of “Solid water” are based on polysaccharide residues [4].

It should be noted that polysaccharide chains in the “Solid water” as well as biomembranes are capable of self-assembly, which corresponds to the minimum of free energy in the systems [6, 7]. Pectins play a certain role in the processes of self-assembly and self-organisation of supramolecular structures in the superabsorbent.

It is known that pectin substances include polyuronides contained in soluble or insoluble forms in all land plants and in most algae. Water-insoluble (at $T = 5–15 \, ^\circ C$) pectin components of plants are called protopectin. In fact, pectin substances are a mixture, and it was possible to separate its soluble part ($25–30 \, %$) from the insoluble one by water evaporation and further dissolution of the dried powder in $70^\circ$ ethanol [8, 9]. The dissolved component belongs to polysaccharides (arabanes) (which hydrolise to 1-arabinose when heated in diluted acids). Pectin substances that are not dissolved in $70^\circ$ ethanol are actually called pectin. The main monosaccharide forming a part of pectin is D-galacturonic acid (Fig. 4).

**Fig. 4.** D-galacturonic acid

In effect, pectin is partially etherified, that is containing [–O–CH$_3$] groups, polygalacturonic acid. Similar to cellulose, as the authors in [8, 9] believe, pectin has chain structure (Fig. 5).

However, such a widespread opinion may be considered somewhat simplified. In a number of cases, pectin chains can be branched (Fig. 6).

The core of the branched molecule (6) has glycosidic linkage $\alpha(1\rightarrow5)$ in the branching point and $\alpha(1\rightarrow4)$ in the branches.

To confirm the scheme presented in Fig. 1, IR spectra of the original superabsorbent from pectin and the superabsorbent after supplementary interaction with polysaccharide

**Fig. 3.** The scheme of water and pectin interaction [5]
were obtained (Fig. 7–9). The obtained results are presented in Table 1. It was confirmed that amides play a significant role in the formation of short-chain fragments in the “Solid water” polymer. Notably, such effect for the original pectin-based polymer is confirmed not only by the presence of amide I absorption bands (3322, 3260, 3185 cm⁻¹) in IR spectra but also by the presence of maximums typical for (C-N and N-H in amides) amide II (1641, 1610, 1464 cm⁻¹) and amide III (750, 669, 550 cm⁻¹) [7, 10–12].

After the interaction with pectin, peaks are observed in the IR spectra of the superabsorbent. These peaks are typical for 6-membered pyranose rings of D-galacturonic acid (1117 cm⁻¹) [7, 10–12].

In the IR spectra of the polymer material there are absorption bands at 1653 and 1609 cm⁻¹ corresponding to stretching vibrations of the C=O group (amide I) and combined frequency of deformation vibrations and the C–N NH group (amide II) of amide fragments [13]. Wide absorption bands at 3184–3332 cm⁻¹ indicate the presence of OH and NH₂ groups of the biodegradable component [11, 14–16]. On the other hand, the superabsorbent (SA) can be characterised as a polymer expressing a bipolar function in the neutral pH region [15–17]. In this case, the polymer network of a “Solid water” sample, formed from polysaccharide units and acrylamide residues, will contain carboxyl groups forming hydration structures with water (ν 3206 cm⁻¹, δ 1653 cm⁻¹ – stretching and deformation vibrations of the OH groups respectively) [15, 16]. Also, short-chain fragments of the “Solid water” polymer contain the residues of –COOH groups not associated with each other or functioning as dimers (1735, 1309, 1240 cm⁻¹) respectively [10, 12].

As for the the supersorbent “Solid water”, plausible guesses can be made about the influence of the pH of medium on water-absorption capacity and swelling of the polymers. The polymer network of “Solid water” samples is formed by polysaccharide units and acrylamide residues, responsible for the presence of amide
Fig. 7. IR spectra of the original superabsorbent (starch+acrylamide+2% crosslinking agent) (1 – 3566; 2 – 3332; 3 – 3184; 4 – 2924; 5 – 2852; 6 – 1653; 7 – 1609; 8 – 1426; 9 – 1351; 10 – 1280; 11 – 1155; 12 – 1080; 13 – 1025; 14 – 988; 15 – 961; 16 – 815; 17 – 621; 18 – 508 cm\(^{-1}\))

Fig. 9. IR spectra of the superabsorbent “Solid water” (pectin + acrylamide + 2 % crosslinking agent), held at 50 °C for 72 hours (1 – 3943; 2 – 3900; 3 – 3881; 4 – 3833; 5 – 3725; 6 – 3587; 7 – 3322; 8 – 3184; 9 – 2924; 10 – 2853; 11 – 2189; 12 – 2162; 13 – 2052; 14 – 1979; 15 – 1744; 16 – 1648; 17 – 1610; 18 – 1454; 19 – 1307; 20 – 1240; 21 – 1117; 22 – 550 cm⁻¹)

Табл. 1. Attribution of absorption bands in the IR spectra of a rare-cross-linked polymer material with superabsorbent and pectin properties

<table>
<thead>
<tr>
<th>n, cm⁻¹</th>
<th>Attribution of absorption bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>3346</td>
<td>ν¹ NH₂ free in amides; ν OH₂···H₂O</td>
</tr>
<tr>
<td>3318</td>
<td>ν OH₂···H₂O</td>
</tr>
<tr>
<td>3260</td>
<td>ν OH₂···O= associ. in primary amides (amide I), ν OH₂···O= associ. with COOH groups</td>
</tr>
<tr>
<td>2941</td>
<td>ν OH₂···O=</td>
</tr>
<tr>
<td>2928</td>
<td>ν C=O in COOH</td>
</tr>
<tr>
<td>2928</td>
<td>ν C=O in COOH</td>
</tr>
<tr>
<td>1641</td>
<td>ν C=N and σ NH in amides (amide II); ν as H₂O</td>
</tr>
<tr>
<td>1617</td>
<td>Amide III; σ-C=O of pyranose rings;</td>
</tr>
<tr>
<td>1518</td>
<td>Fan-shaped CH₃; –COOH in dimers;</td>
</tr>
<tr>
<td>1258</td>
<td>Pendulum σ CH, with –COOH at the end;</td>
</tr>
<tr>
<td>1192</td>
<td>ν OH₂ in 6-membered rings</td>
</tr>
<tr>
<td>831</td>
<td>(CH₃)₃ – pendulum</td>
</tr>
<tr>
<td>687</td>
<td>Amide III; σ CH in rings</td>
</tr>
</tbody>
</table>
and carboxyl groups (Fig. 3). The influence of the OH groups of polysaccharide groups on the formation of hydration structures allows considering moisture absorption as the process of disordering (destruction) of “water-water” associates in all the areas of concentration.

However, in case of maximum moisture absorption, the water structure has to be considered homogeneous, i.e. water molecules are in a single frame with partially filled voids [12, 16]. The presence of carboxyl and amine groups allows considering superabsorbents as ampholytes [15, 16] that can exist in cationic (acidic medium), bipolar (pH = 7), and anionic forms (scheme 1):

\[
\begin{align*}
\text{pH}<\text{pI} & \quad \text{pH}=\text{pI} & \quad \text{pH}>\text{pI} \\
\text{COOH}^- + H^+ & \quad \text{NH}_3^+ & \quad \text{OH}^- + H_3O^+ \\
R & \quad \quad & \quad \quad \\
\text{NH}_2 & \quad \text{COO}^- + H^+ & \quad \quad \text{H}_2O \\
\end{align*}
\]

где pI – изоэлектрическая точка.

The use of the superabsorbent for water retention in different types of soils requires the knowledge of their swelling properties depending on the pH of the medium. For this reason, the ultimate swelling capacity of the samples of various superabsorbents, studied in distilled water (pH = 6.8±0.2) as well as in acid and alkaline media, was determined. Such choice of the condition was due to the fact that soils in which these sorbents may be used are also characterised by a wide range of pH values. The results of the study are presented in Table 2.

### Table 2. Degree of swelling of the superabsorbent sample

<table>
<thead>
<tr>
<th>Superabsorbent</th>
<th>Degree of swelling, ω, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Distilled water</td>
</tr>
<tr>
<td>Solid water, type I</td>
<td>98.90</td>
</tr>
</tbody>
</table>

The presented data shows that all the studied samples have almost the same values of the degree of swelling (ω). However, the value ω for the sorbent “Solid water” is slightly lower in acidic and alkaline environments as compared to the value obtained in distilled water. In this case, water structure is influenced by non-electrolytes (hydroxyl groups of polysaccharide units) and electrolytes (–COO-, Na+, –NH₃+, Cl⁻) [17, 18]. Among the obtained samples of the sorbents “Solid water”, the best results in swelling were achieved with a sample of “Solid water”, synthesised using a hydrophilic crosslinking agent N,N-Methylene-bis-acrylamide. This sample is characterised by the highest values ω in an alkaline medium, which is accounted for by electrostatic repulsion of disassociated carboxyl groups formed as a result of the acrylamide hydrolysis. This makes it suitable for use in leached soils, such as the black soil (Chernozem) in the Voronezh region.

Transition from one ionic form to another occurs with the participation of water molecules and is accompanied by the formation of the first hydration layer (short-range hydration) [18] (scheme 2):

\[
\begin{align*}
\text{R} & \quad \quad \text{COOH}^- + H^+ + H_2O \\
\quad & \quad \quad \quad \text{COO}^- + H^+ + H_2O \\
\quad & \quad \quad \quad \quad \text{H}_2O \\
\text{R} & \quad \quad \text{NH}_3^+ + H_3O^+ + H_2O \\
\quad & \quad \quad \quad \text{NH}_2 + \quad \quad \quad \quad \text{H}_2O \\
\end{align*}
\]

Further water absorption by the sorbent (long-range hydration) occurs due to the formation of H-bonds between the solvent molecules.

One of the possible options of the formation of the polymer frame of the superabsorbent “Solid water” can be related to the formation of SAC-like macromolecules of the complex polysaccharide-acrylamide (AA). If we indicate branch I in the Fig. 10. as X and branch II as Y, the formation of “polysaccharide (pectin)-acrylamide” can be schematically presented in the following way:

The suggested scheme explains to some extent the superabsorbent’s capacity for hydration and absorption of considerable in weight amounts of water [19].

It is confirmed by IR spectra of the original superabsorbent (pectin + acrylamide + 2 % of crosslinking agent) presented in Fig. 9. The specified sample was dried for 72 hours at the temperature of 50 °C. After such a long heat treatment, there are absorption bands 3587; 3322; 3184 cm⁻¹ present in the IR spectra that are typical for stretching vibrations of the OH
groups in hydration structures $\text{H}_2\text{O}--\text{H}_2\text{O}$ (with weak hydrogen bonds); $\text{H}_2\text{O}--\text{HN}$ (with acrylamide fragments) and $\text{H}_2\text{O}--\text{HOOC}$ (D-polygalacturonic acid) respectively [20, 21]. The maximum of 1744 cm$^{-1}$ shows the vibrations C=O in non-dissociated $-\text{COOH}$ groups [11, 15, 16, 21, 22], which is indicative of incomplete deprotonation of carboxyl groups in pectin.

Therefore, the superabsorbent with pectin as the biodegradable component can retain a portion of hydration water even during prolonged drying.

4. Conclusions

1. The samples of the superabsorbent “Solid water” based on acrylamide and N,N-Methylene-bis-acrylamide with addition of pectin were synthesised. One of the options of the formation of macropores in superabsorbents explaining the maximum water absorption was considered.

2. The influence of the content and nature of the crosslinking agent on the product swelling was studied. It was shown that the synthesised polymer material can reversibly absorb up to 500 ml of water per one gram of the product, and the swelling decreases as the degree cross-linking grows. The superabsorbent with pectin as a biodegradable component is able to retain a portion of water of hydration even during prolonged drying.

3. Plausible guesses can be made about the influence of the pH of the medium on water-absorption capacity and swelling of the superabsorbent “Solid water”. The values of the degree of swelling ($\omega$) are almost the same, however, the value $\omega$ for the sorbent is slightly lower in acidic environments as compared to the value obtained in distilled water. This polymer is also characterised by the highest values $\omega$ in an alkaline medium, which is accounted for by electrostatic repulsion of disassociated carboxyl groups formed as a result of the acrylamide hydrolysis. This makes it suitable for use in leached soils, such as the black soil (Chernozem) in the Voronezh region.

4. IR spectroscopy allowed determining the presence of functional groups of the superabsorbent participating in the formation of supramolecular structures containing linked water molecules. As a result, this leads to the self-organisation elements of the system.

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Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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