Water retention in different types of protective gel compositions for plant rhizosphere

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Abstract. The research investigates thermodynamic characteristics of water-retention capacity in different types of high swelling polymer hydrogels mixed with mineral soil substrates. The use of a combination of methods of equilibrium centrifugation and thermodesorption of soil moisture allowed for the first time to estimate the water-retaining curves and dispersion of gel compositions in the range of absolute values of thermodynamic potentials from 0 to 1 million J/kg. The introduction of hydrogels in concentrations of 0.1-0.3% total weight of the enclosing mineral material leads to a 5-15 fold increase in the total energy of water retention, 3-8 fold increase in water capacity and available moisture range, bringing investigated hydrophysical characteristics of the original sandy substrate at the level of the fertile loamy soils. The new types of acrylic hydrogels with amphiphilic fillers obtained by the author's technology had a greater water-holding capacity and a better structuring effect in comparison with the "Aquasorb" European trade mark. The incorporation of the electrolyte additives in the form of trace elements and ionic silver into the polymer matrix practically does not change the swelling capacity, allowing adding elicitor and antimicrobial properties to these compositions without compromising the effect of water retention.

1. Introduction

The modern practice of intensive agriculture extensively uses natural and synthetic polymeric materials to improve unsatisfactory soil properties and its fertility. Special attention in this area is paid to new promising materials-soil modifiers with nanostructural organization. These modifiers, even in small doses, are capable to radically change the physical state of the soil. A new generation of moisture scavengers (super absorbents) in the form of strongly swelling polymer hydrogels (SSPHs) can be considered as such soil modifiers [1-8]. These substances of synthetic origin have a very high degree of swelling in pure water (up to 1000 g H2O/g of dry polymer) and may be an effective means of regulating water retention, especially for widespread light-textured soils. There are interesting attempts to use them not only to improve the water-physical properties and soil structure, but also as carriers of plant mineral nutrition elements and modern plant protection agents in the plant rhizosphere [8-10]. However, the use of SSPHs is constrained by the lack of quantitative information on the effectiveness of polymers doses, considering the specifics of different soils, their structural organization, edaphic factors of possible suppression of swelling of gels and their biodegradation, and ultimately – by the lack of clear scientifically-based technological regulations in this area. Their
development should be based on modern models of the energy-mass exchange in the system "soil-plant-atmosphere". For this purpose, it is necessary to have quantitative information about water-retention characteristics (WRCs) in the form of thermodynamic soil water potential functions [5, 6], which describe soil substrates and their compositions with hydrogels.

Hence, the main objective of the study was to quantify the WRCs of gel compositions with the mineral sandy substrates, including new types of SSPHs synthesized by the technology, developed by the authors. The new compounds include in the polymer matrix both amphiphilic components in the form of humates and a dispersed peat, as well as electrolyte additives in the form of trace elements and ionic silver [11, 12]. Due to the possible use of SSPHs as a carrier of mineral nutrients and plant protection products we additionally investigate the influence of trace elements and ionic silver additives in the gel composition on their WRCs. For the first time in soil physics, the combined method of centrifugation and thermodesorption of water was used to obtain water retention curves. This new method allowed to expand the range of thermodynamic soil water potential up to 1 million J/kg.

2. Objects and methods

The tested materials included several types of a new generation of acrylic SSPHs for agriculture, floriculture, gardening and landscaping. The first sample (№1) is well-known "Aquasorb" European (France, Germany) trade mark with a maximal degree of swelling in pure water (700–1000 kg H₂O/kg). It was compared with innovative products of the Ural chemical factory (Russia) by patented author's technologies [11, 12]. These new products included various compositions of acrylic copolymers based on acrylamide and acrylic acid salts, filled by wastes of biocatalytic production of acrylamide, salts of humic acids in an aqueous paste as well as dispersed peat with additives of ionic silver. Methylene-bis-acrylamide was used as a crosslinking agent. Hydrogel VUM-ITH (sample №2) is the base co-polymer of acrylamide and ammonium acrylate filled (28%) by solid wastes of a biocatalytic production of acrylamide as a mixture of microbial cells, cell agglomerates and filtroperlit. This hydrogel has a water absorption of 350 kg H₂O /kg of granules in sizes from 1 to 5 mm. Sample №3 (VUM-H) includes, in addition to biocatalytic wastes (12%), humates of potassium and sodium in an amount of 8% of dry matter and is characterized by water absorption up to 370 kg/kg. Composition of VUM- HMC hydrogel (sample №4) is similar to the previous one, but with the addition of magnesium and zinc (the trace elements of mineral nutrition), 0.4% in terms of metals. The water absorption of the hydrogel is 340 kg/kg. The last two samples №5 (VM-P) and №6 (VM-P Ag), along with the co-polymer of acrylamide and sodium acrylate, contain a finely dispersed peat as a filler (23.5%) and 0.1-1% of additives of an ionic silver. In contrast to the previous work [7], silver and trace elements were incorporated directly into the polymer matrix during the synthesis of hydrogels. This new technology needs patent protection and cannot yet be published. Samples №5 and №6 were characterized by a black color, which is not typical for hydrogels, and by the limiting degree of swelling in distilled water near 500 kg /kg.

The mineral soil substrate was represented by two samples of a medium-grained and fine-grained quartz sands. The mineral-gel compositions contained from 0.1 to 0.3% of SSPHs by weight of the mineral substrate. For their preparation, the calculated amount of dry SSPH was placed in a measuring cup, which then was filled with distilled water in the amount required to saturate a given weight of sample soil substrate to a state of full (total) water capacity. After swelling, the gel substance was mixed with mineral soil substrate, to achieve a uniform distribution in the host material. Otherwise, in the case of mixing of a dry gel, its uniform distribution in the sandy substrate is virtually impossible because of the low doses of SSPHs, not exceeding 0.3 g per 100 g of the mineral mass. All compositions were prepared and studied in 3-fold replicates.

Thermodynamic analysis of water-retention capacity of mineral samples and their compositions with hydrogels was carried out by combination of equilibrium centrifugation in the author's modification [13] with a new method of soil water thermodesorption [14]. Unlike the well-known Ioffe-Gradner formula used in soil sciences for assessing the pressure (potential) of water during
Figure 1. WRCs (main figure) and pore distribution (inset) of mineral-gel compositions under the impact of "Aquasorb" hydrogel: A - 0.1%SSPH; B - 0.2%SSPH; C - 0.3%SSPH; 1 - sandy substrate; 2 - hydrogel composition; lines - models (3), (5); dashed lines - Voronin secants; equations - model (3).
centrifugation, our modification included the gravitational component, which allowed to build the WRC from the state of full saturation [13]:

$$|\Psi| = \Psi_{\text{dry}} - \Psi_{\text{wet}} = -\left(0.011 \cdot n \cdot r \cos(\alpha) + g \sin(\alpha)\right) \cdot h,$$

where \(n\) [rpm] is the number of centrifuge revolutions per minute, \(r\) [m] is the distance from the rotation axis to the mass centre of the sample, and \(h\) [m] is sample’s height, \(\alpha\) is the angle between the horizontal axis and the central symmetry axis of the sample; \(|\Psi|\) and \(\psi_{\text{dry}}\) are absolute values of soil water pressure and potential in porous media, both having negative sign by definition. We use a high-speed laboratory centrifuge Hettich Universal 320 (Germany) with a water-retention energy range (soil water potential or equivalent soil water pressure according (1)) from 0 to 3030 J/kg (kPa).

After the last stage of centrifugation (12000 rpm), the samples were placed for differentiated drying at temperature levels of 30, 40, 50, 60, 70, 80, 105 °C into a KD 200 drying oven (China) with a forced circulation and ventilation of air and simultaneous control over relative air humidity and temperature using DS 1923 "hygrochron" programmed electronic sensors [14]. This simple procedure estimates WRC in the range of absolute values of the thermodynamic potential of soil water from 3020 to 1000000 J/kg, as well as specific surface area according to our methodical developments [14]. In a thermodynamic tank of laboratory with a constant air humidity (\(f\)) and temperature (\(T\)), the water potential depends linearly on the temperature in the drying oven (\(T\)) by the fundamental thermodynamic equation, obtained in [14]:

$$\Psi = Q - m \cdot T,$$

where \(m = \{Q/T, - R \cdot \ln(f)/M\}, \ Q = 2401 \pm 3 \text{kJ/kg}\) is specific heat of evaporation for the temperature range of 0-100°C, \(R = 8.314 \text{J/(mol·K)}\) is universal gas constant, \(T\) [K] is an absolute temperature in the drying oven, \(M = 0.018 \text{kg/mol}\) is the molar mass of water. In a dry room at relative humidity \(f=0.2-0.3\) and absolute temperatures \(T_{\text{r}}=291-293 \text{K}\) drying at 105 ° C gives, in accordance with (2), the value of the thermodynamic potential of water in the range of 895-999 kJ/kg or near 1 million J/kg.

Thus, the combined method of centrifugation and thermal desorption of water gives the opportunity to estimate the energy of water retention in the entire range of water content from saturated to absolute dry state of the soil. In the case of hydrogel compositions intended to save water in arid conditions, a particularly valuable advantage of the method is the possibility of obtaining information about water retention in the area of low and medium humidity values, where the surface molecular forces of gel structures dominate over the capillary phenomena in porous media [15]. In addition, the method allows to estimate the effective specific surface area (\(S\)) of the gel compositions in two independent ways - according to the theory of Brunauer-Emmett-Teller (\(S_{\text{BET}}\)) after the transformation of the WRCs to the desorption isotherms [14], and directly by the slope of the WRC in semi-logarithmic coordinates (\(S_{\text{WRC}}\)), in accordance with the fundamental ion-electrostatic model of disjoining pressure, as proposed in [15]. This model looks like:

$$|\Psi| = a \cdot \exp \left( - \frac{W}{S \rho \lambda} \right) = a \cdot \exp \left( - bW \right),$$

where \(b\), kg/kg is the physically based parameter controlled by the dispersion and the electric double layer (EDL) properties, \(a\) [J/kg] is the physically grounded parameter reflecting the surface shape and potential (charge), \(S\) [m²/kg] is the variable effective specific surface of the interphase boundary, \(\rho\) [kg/m³] is the water density, \(\lambda\) [m] is the effective Deby EDL thickness. In a standard stable state with a minimum water film thickness \((h_{\text{st}} = 2\lambda_{\text{st}})\), the effective specific surface area (\(S_{\text{WRC}}\)) is defined by the slope of the WRC as [15]:

$$S_{\text{WRC}} = \frac{1}{2\rho \lambda},$$

where \(r = 1.38 \cdot 10^{-10}\) m is a crystallochemical radius of water molecule.

Approximation of WRC experimental data in the range of dominance of capillary forces has been performed with the van-Genhuceten model [16]:
\[ W = W_s + \frac{(W_s - W_r)}{(1 + (\alpha |P|)^m)^n}, \]  

where \(|P|\) is an absolute value of soil water pressure (potential), \(W_s\) is residual moisture content corresponding to a tightly bound water, \(W_r\) is water content in a state of saturation of the soil (full water capacity), \(\alpha, n, m\) - empirical constants, and \(m = 1 - 1/n\).

Evaluation of parameters \(a, b, W_s, W_r, \alpha, n\) in models (3), (5) according to experimental data of WRCs was carried out by the application "Regression Wizard" in the program S-Plot 12 version. Additionally, we propose the algorithm to assess specific indicators of a physical system "soil-gel" and structural curves of pore distribution according to their size using the algebraic differential and integral analysis of the WRC, approximated by the van-Genuchten function (5). Calculation of the values of field water capacity (FWC), the maximum molecular water capacity (MMWC) or moisture of capillary bond break, wilting point (WP) and the maximum adsorption capacity (MAC) by Voronin’s method [17]. It is based on the use of the next secant equations in the form of pressure (by its modulus) as a function of water content: \(|P|=10^{1.17+0.8W}\) for FWC, \(|P|=10^{1.17+3W}\) for MMWC, \(|P|=10^{4.2+3W}\) for MAC and \(|P|=1500\) kPa for WP. The formula corresponding to the difference between the function of the matrix potential (pressure) from the van-Genuchten model (inverse to (5) function) and one of the above equations by Voronin’s secants has been written as a computer program realized in MS Excel 2007. Using the routine "Selection Parameter" of Excel, from its "Tools" menu, the desired moisture value at which the pressure difference becomes zero is obtained. This value is determined by the abscissa of the intersection point of Voronin’s secant with WRC. The proposed algorithm, having a high speed and accuracy, favorably differs from a traditional graphical analysis.

An additional indicator - the capillary water capacity (CWC) as a conditional boundary between the capillary and gravitational water in the physical system "soil-gel" was defined as the inflection point of the van-Genuchten function [13, 18]. An analytical condition of the inflection point as a zero of the second derivative of the function (5), in the most common simplification of the van-Genuchten formula, viz. \(m = 1-1/n\). is expressed by the formula:

\[ \text{CWC}= \{(m+1)^{-n}\}(W_s-W_P)+W_s. \]  

Note that the obtained inflection point of the WRC (6) differs from the proposed in [18]. The critical analysis of [18] shows that the author examined not a real, but "visual" effect of the inflection of the van-Genuchten function on a logarithmic scale. The condition of the inflection point of the pF-curve, rather than of the WRC function was found in [18]. The real singular point for WRC is found from our proposed expression (6).

A differential analysis of WRC in the form of the van-Genuchten model was used to calculate the structural pore size distribution curves as a basic indicator of soil physical quality, according to [13, 18]. For this purpose, the first derivative of the function (5) or the so-called differential water capacity of the soil [18], reflecting pore volume of a certain size category, was multiplied by the pressure at which this category has drained. It should also be noted that the formula (5) characterizes not the bulk moisture, as it is necessary to calculate the pore volume, but the degree of saturation of the effective pore space (without the tightly-bounded moisture). Therefore, after differentiation of (5), the resulting value of the differential water capacity \(dW/dP\) was multiplied by the soil bulk density \((\rho_s)\) and the difference \((W_s-W_r)\). After simple calculations we obtained the following formula for calculating the pore volume distribution by the size of their radii \(V(r)\) from the of van-Genuchten model:

\[ V(r) = (n-1)(W_s-W_r)\rho_s\left(1+(\alpha P)^m\right)^{-m-1}(\alpha P)^n \]  

Together with a differential analysis of WRC, the opposite procedure of integration has been used. An integral water-retention energy indicator in the capillary region \((E, [J/kg])\) numerically equals to the area under the WRC curve in a fixed moisture range \(W_s\leq W \leq W_r\) [13]:

\[ E = \int_{W_s}^{W_r} \psi \ dW, \]
Figure 2. WRCs (main figure) and pore distribution (inset) of mineral-gel compositions under the impact of VM-P hydrogel: A; B; C - see legend of figure 1; 1 - sandy substrate; 2 - pure hydrogel composition; 3 – 0.1%Ag; 4 – 1%Ag in SSPH matrix; lines - models (3) and (5).
The physical meaning of the parameter $E_r$ comes from its dimension J/kg of solid phase and corresponds to a specific energy from the solid phase of the soil moisture retention in the selected range. As an analytic expression of the integral (8) for the van-Genuchten function was difficult, we used a numerical method of trapezoids with the implementation in MS Excel 2007 as a macros (the author is M.V. Glagolev). Thus, as the lower limit of integration, the total water content (humidity of saturation $W_s$) was selected. The upper limit of integration – was a nominal minimum humidity value ($W_e$) at a fixed potential absolute value $\nabla i l e = 3000$ J/kg.

One more integral indicator – the total energy of water retention from the surface of the solid phase ($E_r,[J/kg]$) was calculated as an analytical integral of the equation (3), according to [15]:

$$E_r=a/b.$$ (9)

For all calculations the corresponding algorithms in our MS Excel 2007 computer program have been made, allowing for analysis of indicators of physical condition and the structural organization of the test gel compositions. The following section discusses the results of this comparative analysis on a standardized system of indicators based on the modern concept of the thermodynamic state of soil physical systems [13, 15, 17].

3. Results and discussions

Figures 1-3 show the WRCs and the structural curves of distribution of pores relatively to their size calculated by WRCs for the tested gel compositions. In table 1, we placed traditional agrophysical parameters of water capacity, the available soil water range ($AWR = FWC-WM$), indicators of the integral energy of water-retention, and indicators of the effective specific surface area estimated by the BET method and by the slope of WRC. All tested hydrogel compositions were characterized by a stable increase in water-retention in proportion to a dose of the preparation over a wide 0 - 1000 kJ/kg range of absolute soil water potential (pressure) values. WRCs of gel compositions have been regularly shifted right regarding the control position (mineral substrates), which indicated an increase in energy of water-retention and moisture capacity of samples. Pore sizes spectra, in opposite, exhibited a tendency of moving left towards smaller sizes. Such tendency, we believe, reflects an effect of aggregation of the mineral mass by hydrogels. Besides, in its greatest extent, the effect manifests for the high doses of 0.3% and for hydrogels of the Ural chemical factory with amphiphilic (peat, humates) fillers. Shifting of the maxima on the structural curves was accompanied by a decrease in the radius of the dominant pore from 100-330 microns in the original coarsely dispersed substrates up to 15-30 microns in amphiphilic compositions of VUM-H, VUM-HMC, and VM-P with humates and peat, up to 60 microns in the base VUM-ITH sample with biocatalytic wastes, and up to 30-60 microns in standard "Aquasorb" preparation. At drying samples, their aggregate structure (0.3% dose) was manifesting in the form of solid lumps of a mineral mass cemented with hydrogel.

Field water capacity ($FWC$) at SSPHs doses of 0.2-0.3% from the soil dry weight constituted 15-25% comparing to 3.3-4.6% in sandy substrates, that means that the water-retention capacity in such doses increased 5-8 (even up to 9) times corresponding to translation of the original sandy substrates in the loamy soil by this indicator. Along with that, the increase in the wilting point ($WP$) rarely exceeded 2-5 times. As a result, the soil water range available for plants ($AWR$), under the influence of hydrogels, was expanding 4-8 (up 10 - 13) times as compared to the original mineral substrates (table 1). We note that according to this indicator, being important from the agrophysical point of view, the new amphiphilic sample of VM-P with a peat filler has shown the best result for the low concentration of 0.1% among the products of the Ural chemical factory. $AWR$ constituted 13-15.4% vs. 1.6-3.3% in sandy substrates, and 4-6.6% in the other innovative products samples, reaching the level of the European brand "Aquasorb" ($AWR =12-15\%$) with fully hydrophilic properties and the maximal degree of swelling in pure water.

The capillary water capacity ($CWC$) indicator was increased not so considerably under the 0.1-0.3% SSPHs – no more than in 1.6-2.3 times in comparison with the $CWC$ of the original mineral substrates. At this, the difference between the total water capacity and $CWC$, reflecting the amount of free gravitational water being not preserved by soil, was steadily declining from 4.5-5.7% in control.
Figure 3. WRCs (main figure) and pore distribution (inset) of mineral-gel compositions under the impact of different SSPHs: A - VUM-ITCH hydrogel; B - VUM- H hydrogel; C - VUM- HMC; 1 - sandy substrate; 2 - 0.1% SSPH; 3 - 0.2% SSPH; 4 - 0.2% SSPH; other designations - see figures 1, 2.
substrates, to 1.2-3.0% at the SSPHs 0.2-0.3% doses, and to 3-4% at a dose of 0.1%, except for the new amphiphilic VUM-H, VUM-HMC, and VM-P samples, where the difference, even at low concentration, did not exceed 2.5-3.2%. All together indicates a very small proportion of the free gravitational water in gel compositions and, consequently, highlights the dominance of capillary mechanism of water-retention and mass transfer of the main amount of mobile water (CWC-MMWC), which reaches 20-30% in the disperse systems being studied. This result is of significant technological importance for designing water accumulative soil constructions based on SSPHs, where the focus should be emphasized not on resolving the problem of lost for deep percolation, but rather on an issue of capillary absorption of water in the subsoil. In our work, for this purpose we recommend applying crushed stone screens or silicone water-repelling agents that block the capillary effect and the unproductive water losses associated with it, as well as secondary salinization of the root layer zone (plant rhizosphere) [6].

The maximum molecular water capacity (MMWC) indicator, to which, in the classical agrophysics, a break of capillary denseness and termination of transmission of hydrostatic pressure in the soil are related, increased 2.5-3.7 times at the SSPHs concentration of 0.1%, and 4.3-7.4 times at higher doses of 0.2-0.3%. This result can be interpreted as an appropriate increase of soil water available to plants, but not actually exposed to unproductive outflow into the soil moisture (MMWC-WM) under the influence of SSPHs. The MMWC/FWC ratio in the studied gel compositions was consistently equal to 0.8-0.9, thus exceeding the classical value of 0.7 generally used for calculation of the lower limit of irrigation rate (0.7 FWC). This can be attributed either to drawbacks of the Voronin method [17], which understates the FWC value for coarsely dispersed soils, or to variability of the FWC value itself and its dependence not only on the properties of solid phase and pore space of the dispersed system, but also on the depth of a pendulous water body, according to [13].

The MAC parameter indicates the value of a stationary (i.e an analogue of the solid phase) strongly bound water in the soil, necessary for the correct simulation of water movement in a porous system. The relatively small changes of the MAC (in 2-2.5 times at a dose of 0.1% and in 3-5 times at higher concentrations) can be interpreted as an insignificant increase in the fixed volume of water in coarse porous media and hydraulic resistance to mass transfer under the influence of SSPHs.

In this regard, the fact of a significant increase in the effective specific surface area of mineral substrates under SSPHs impact looks somewhat unusual, since, according to [17], MAC is closely correlated with the water content of the monolayer by BET. In reality, the effective specific surface area of the studied gel compositions increases 3-3.8 times at SSPH concentrations of 0.1% and up to 6.0-10.2 times at higher doses of SSPH of 0.2-0.3%, reaching the values of 40-60 m²/g (up to 75 m²/g), typical for light and medium loams. Note that the effective specific surface area estimated by the standard BET method actually coincided with one estimated by the slope of WRC (formula (4)) proposed in [15] on the basis of the fundamental ion-electrostatic model (3) of disjoining pressure, as follows from the analysis of figure 4. This fact confirms the universality of the new methodology for assessing the specific surface area and its suitability not only for soils, but also for soil modifier materials, including synthetic hydrogels.

The indicator of the integral water-retention energy (E₁) of pore space of the tested compositions in the capillary area distinctly reflected all the above mentioned patterns of increase in water-retention capacity of the soil substrate affected by different SSPHs concentrations. The dose of 0.1% has increased this indicator 5-10 times (up to 9-15 times in the case of a new amphiphilic VM-P sample with a peat filler). At higher (0.2-0.3%) SSPHs doses, the integral water-retention energy increased 10-20 times (up to 20-30 times in VM-P and "Aquasorb" preparations) (table 1).

Changes in the total water retention energy (E₆) from the surface of the solid phase, estimated by model (9), were less contrasting. This value increased 1.5-2.2 times at low doses of 0.1% SSPHs and up to 2.3-5.5 times at higher concentrations of 0.2-0.3% SSPHs. A comparison of trends in E₁ and E₆ parameters clearly indicates the dominance of the bulk rather than surface water absorption mechanisms in the gel compositions under the influence of the SSPHs.
| SSPHs rates %: | CWC | FWC | MM | WP | MAC | AWR | Ec, J/kg | Et, J/kg | Swrc m²/g | S_bet m²/g |
|--------------|-----|-----|----|----|-----|-----|----------|----------|------------|------------|
| 0% | 21.8 | 4.6 | 4.0 | 1.3 | 1.3 | 3.3 | 3.6 | 2033.0 | 7.4 | 8.0 |
| "Aquasorb" hydrogel. | 0.1% | 34.6 | 19.2 | 14.7 | 4.2 | 3.1 | 15.0 | 39.6 | 3049.7 | 27.4 | 31.0 |
| 0.2% | 46.0 | 26.0 | 20.2 | 8.3 | 5.3 | 17.6 | 81.4 | 6517.4 | 47.8 | 51.1 |
| 0.3% | 45.1 | 28.5 | 22.4 | 9.8 | 5.1 | 18.7 | 99.8 | 11105.7 | 64.0 | 63.6 |
| Monomineral quartz sand (control-1) | 0.1% PM | 33.8 | 18.6 | 14.6 | 4.0 | 2.5 | 14.5 | 47.9 | 4212.1 | 26.5 | 26.9 |
| 0.1% +Ag 0.1% | 31.6 | 17.0 | 13.4 | 4.1 | 3.2 | 12.9 | 32.3 | 3573.3 | 28.2 | 30.0 |
| 0.2% +Ag 1% | 35.6 | 19.5 | 15.3 | 4.1 | 2.2 | 15.3 | 52.8 | 3050.6 | 26.0 | 23.3 |
| 0.3% +Ag 0.1% | 37.6 | 23.7 | 18.3 | 5.8 | 3.2 | 17.9 | 68.3 | 5073.3 | 36.1 | 35.0 |
| VM-P hydrogel | 0.2% | 37.3 | 22.7 | 18.1 | 6.6 | 3.6 | 16.1 | 75.3 | 5836.3 | 42.5 | 45.1 |
| 0.2% +Ag 1% | 34.7 | 21.6 | 16.6 | 6.9 | 5.9 | 14.6 | 43.9 | 7685.9 | 44.4 | 42.3 |
| 0.3% +Ag 0.1% | 49.1 | 28.6 | 22.2 | 9.5 | 5.3 | 19.1 | 93.2 | 9726.3 | 56.8 | 55.0 |
| VUM-ITCH hydrogel | 0.2% +Ag 1% | 45.9 | 27.4 | 21.7 | 9.9 | 5.7 | 17.5 | 88.9 | 11087.2 | 53.5 | 55.2 |
| 0.3% +Ag 1% | 46.8 | 29.0 | 22.7 | 9.6 | 4.5 | 19.4 | 109.4 | 7986.5 | 53.0 | 52.4 |
| Monomineral quartz sand (control-2) | 0.1% | 24.8 | 3.3 | 3.1 | 1.7 | 1.7 | 1.6 | 4.6 | 1972.9 | 7.1 | 8.0 |
| 0.1% +Ag 0.1% | 35.1 | 10.2 | 9.1 | 3.6 | 2.8 | 6.6 | 23.1 | 3752.8 | 22.6 | 24.5 |
| 0.2% +Ag 1% | 51.8 | 20.7 | 17.9 | 9.6 | 5.8 | 11.1 | 69.4 | 5630.0 | 62.7 | 62.9 |
| 0.3% +Ag 1% | 48.1 | 28.4 | 22.9 | 9.5 | 6.4 | 17.0 | 98.8 | 6660.8 | 75.2 | 73.3 |
| VUM-H hydrogel | 0.2% | 46.1 | 8.6 | 7.9 | 4.5 | 4.1 | 12.6 | 3773.0 | 23.8 | 23.7 |
| 0.3% | 47.4 | 16.7 | 14.8 | 7.2 | 4.3 | 9.5 | 55.6 | 5651.7 | 45.7 | 47.0 |
| VUM-HMC hydrogel | 0.3% | 45.5 | 28.1 | 22.3 | 9.7 | 4.7 | 18.3 | 107.3 | 6660.8 | 75.2 | 75.0 |
| 0.1% | 52.6 | 9.4 | 8.5 | 4.6 | 4.1 | 4.8 | 16.2 | 4561.4 | 25.6 | 28.2 |
| 0.2% | 51.0 | 15.2 | 13.3 | 6.2 | 4.0 | 9.0 | 7.7 | 4586.6 | 39.1 | 37.5 |
| 0.3% | 50.9 | 29.7 | 23.0 | 9.5 | 4.4 | 20.2 | 71.2 | 6666.4 | 56.6 | 59.6 |

**Figure 4.** Comparative analysis of two methods for evaluating the effective specific surface of gel compositions (explanations are in the text).
The usage of amphiphilic fillers (humates, peat) in the production of the Ural chemical factory did not significantly change water retention properties of gel compositions. We can draw a similar conclusion concerning insignificant changes in water retention by comparing amphiphilic variants supplemented or not with electrolytes’ admixtures (VUM-H and VUM-HMC). Inclusion of ionic groups of electrolytes in the acrylates and humates form in the structure of a polymer matrix allows us to solve the problem of reducing the SSPHs swelling as affected by the osmotic stress [5]. In this case, embedded cations can react in ion exchange and serve as a source of elements of plants’ mineral nutrition. Indeed, the maximum degree of swelling of the gel in the substrate with the total moisture capacity (porosity) \( W_{c}=30-50\% \) at SSPHs doses \( C=0.1-0.3\% \) is limited to the value of \( W_{s}/C \), not exceeding 300-500 kgH\(_2\)O.

As the experiment with the samples of VM-PAg amphiphilic gel at a dose of 0.1-1% silver shows, the compositions based on it also did not worsen much the water retention, dispersion and structural properties, which remained at the level of "Aquasorb" European preparation in the same concentrations 0.1-0.3% SSPHs (figures 1-2; table 1), despite the lower degree of free swelling than hydrophilic gel brand "Aquasorb", was just as effective as Aquasorb in soil water retention. This fact is quite understandable because in the limited pore space weakly cross-linked hydrogels are unable to realize their full properties of maximum swelling [5]. Super swelling up to 1000 kg/kg for soils is useless, which we considered when developing innovative technologies for the synthesis of filled hydrogels [11, 12].

The introduction of silver into the polymer matrix, on the one hand, protects the hydrogel from rapid biodegradation in soils, and, on the other, allows the use of such compositions as modern plant protection agents directly in the plant rhizosphere. Our previous work has shown high efficiency of rhizosphere gel compositions based on ions and silver nanoparticles for protection against major potato pathogens, including late blight [8]. However, in [7, 8], the method of introducing silver in the form of true and colloidal solutions for swelling of gels was used, which is problematic from a technological point of view. The new VM-PAg preparation, while maintaining high water-retention properties, already contains silver in its composition in amounts of 10-100 ppm in a state of complete swelling sufficient to suppress the main plant pathogens, according to [8, 19-22]. Realization and field investigation of such water-holding and antimicrobial protective compositions for potato rhizosphere is planned within the further development of this work.

4. Conclusion
In summary, we can conclude that the analyzed hydrogels appear to be an effective facility of improving the water-retention capacity of coarsely dispersed soil substrates. The new technology of filling polymer matrix with amphiphilic agents allows us to inject them with various substances, including stimulants and inhibitors of the biological activity without substantial damage to the main water absorption function, and thus to regulate the intricate set of biophysical processes inherent to the soil.

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