Thermodynamic evaluation of the impact of strongly swelling polymer hydrogels with ionic silver on the water retention capacity of sandy substrate

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Abstract. The impact of two types of strongly swelling polymer hydrogel (SSPH) on the water retention capacity of quartz sand in pure water and Ag⁺ solutions (10⁻¹⁰⁻¹⁰⁻² mg/l) has been studied by using a centrifugation method in a wide range of thermodynamic water potential (Gibbs energy) from 0 to 3030 J/kg. The experimental data for the water retention curves (WRC) were estimated by the van Genuchten model. Both hydrogels – the Aquasorb preparation (Germany) with hydrophilic properties and high degree of swelling in pure water (700–1000 g H₂O/g) and the new Russian amphiphilic SSPH with a peat filler (degree of swelling 500–700 g H₂O/g) were very effective as water adsorbing soil conditioners in relatively small doses from 0.05 to 0.3% per mass of dry (105°C) soil substrate. The water retention capacity of sandy substrate increases under the influence of SSPH with 2–3 times up to the level of native loamy sands and loams. Adding Ag⁺ to the water solution results just for the highest concentration of SSPH (0.3%) and iconic silver (100 mg/l) in a significant decrease of the water retention in the soil-gel compositions.

1. Introduction
A new generation of synthetic materials – strongly swelling polymer hydrogels (SSPH) belong to a class of super water absorbers and are used in agricultural melioration practices, gardening and landscaping to improve soil water-holding capacity and structure [1-8]. The high water retention capacity of the SSPH is used, which is characterized by an equilibrium free-state swelling up to 700-1000 g H₂O per gram of soil substance. However, the soil as biologically and chemically active porous media has negative impact on the SSPH due to biodegradation, osmotic stress, limited pore space, envelope pressure, etc. These factors can strongly decrease the SSPH efficiency in the soil that requires the development of more suitable and resistant media materials. Incorporating the monogenic groups into the polymer matrix causes a blockade of the osmotic mechanism of the gel’s swelling decrease (destruction of the ion-electrostatic barrier), according to [1]. In addition, we suggest to fill the polymer matrix by natural amphiphilic components like humates or peat, that increases the resistance of SSPH to microbial destruction in the soil on one side and improves their quality as structural agent and effective lock of microelements and crop protector in the root zone on the other [9]. This research compares a new type of acryl SSPH filled by peat with traditional hydrophilic preparation (trade mark “Aquasorb”) in pure water and Ag⁺ solution as microbial inhibitor and crop protection agent.
It is clear that an increase in water-holding capacity by SSPH of one soil layer is insufficient for optimization of its moisture regime, since the latter is dictated by water movement in the entire profile, together with the water influx and discharge (evapotranspiration) rates. Consequently, for proper evaluation of the efficacy of the SSPH, as well as any other soil conditioner, a system analysis of of water and polymer behaviour in a given soil-bioclimatic condition is required. Such analysis is conveniently achieved using a computer model of water transfer in soils affected by SSPH, which should account for the properties and dynamics of the polymer as well [4]. A central part of the computer models (see for example HYDRUS-1D [10]) is a hydraulic block, which requires input data on the changing soil water-retention curve (WRC) or the dependences between soil moisture and thermodynamic potential of soil water (specific Gibbs energy) affected by SSPH. So in the current research, special attention is paid to instrumental evaluation of WRC in the soil substrate and its alteration affected by SSPH. The objective was, besides collecting experimental results of WRC as a function of the doses (concentration) of SSPH in soil substrate, to estimate the WRC by the standard van Genuchten model using in contemporary computer media for the modelling of energy and mass transfer in soils [11]. Thus determination of WRC as a basic thermodynamic characteristic of the “soil-gel” system allows not only comparison of different types of SSPH but also obtains important information for the future technological modelling the water accumulative soil construction based on SSPH [4].

2. Materials and methods

The tested materials included two types of SSPH: the first sample (№1) is well-known in floriculture and gardening, namely acryl hydrophilic Aquasorb preparation (Germany) with high degree of swelling in pure water (700–1000 g H₂O/g) and the second sample (№2) is the new Russian amphiphilic acryl SSPH with a peat filler and medium degree of swelling (500-700 g H₂O/g) [12]. The new product (sample №2) along with the co-polymer of acrylamide and sodium acrylate contains as filler (23.5%) finely divided (less than 0.25 mm) peat; it has not characteristic for the SSPH black colour. Soil substrate in experimental studies served as the sample monomineral medium-grained quartz sand (so-called white “glass sand”) was used. The SSPH doses 0.05; 0.1; 0.2; 0.3% per dry mass of mineral soil substrate were used. The experiments were conducted in pure deionized water and in water solutions of 10-100 mg/l Ag⁺ in nitrate form. It is assumed that incorporation of Ag⁺ can protect SSPH as well as the root zone in case of SSPH application from adverse microbial activity and pathogenic microorganisms. The samples were prepared by placing a calculated amount of dry SSPH in a measuring cup, which then was filled with distilled water or Ag⁺ solution; the amount required to saturate a given soil substrate sample weight to a a state of full capacity (water saturation). After swelling the gel substance was mixed with mineral soil substrate, allowing it to achieve a uniform distribution in the host material. Otherwise, (in the case of mixing dry gel) it is virtually impossible because of the low doses of SSPH, not exceeding 0.3 g per 100 g of the mineral mass. All compositions were studied in 3-fold replicates.

Thermodynamic analysis of water-retention capacity of soil samples and their compositions with hydrogels was carried out by equilibrium centrifugation with author’s modification [13] with a high-speed laboratory centrifuge Hettich Universal 320 (Germany) with a water-retention energy range (soil water potential or equivalent soil water pressure) from 0 to 3030 J/kg (kPa). With the centrifugation method water was removed from the sample under the effect of centrifugal force. The developed pressure on the liquid phase (P) or equivalent of soil water potential in first approximation (small or so-called undistributed samples) can be determined from the equation [13]:

\[ P = \rho_\ell \omega^2 R h \]  

(1)

where \( \omega \) is the rotation speed, \( \rho_\ell \) is the liquid’s density, \( R \) is the distance from the rotation axis to the mass centre of the sample. The construction of the high-speed Hettich centrifuge involves an inclined position of the sample with respect to the rotation axis; therefore, a correction factor \( \cos(\alpha) \), where \( \alpha \) is the angle between the horizontal and the central symmetry axis of the sample, should be included in Eq. (1). For low speeds regimes of the centrifuge, the gravity component of the pressure
\( P_e = g \cdot h \cdot \sin(\alpha) \), where \( h \) is the sample’s height, and \( g \) is the acceleration of gravity) should be taken into consideration. The rotation speed (\( \omega \)) is calculated from the number of centrifuge revolutions per minute (\( N \)) using the equation \( \omega = \pi N / 30 \), where \( [\omega] = s^{-1} \). Therefore, the final equation for determining the absolute values of the soil water pressure (or equal potential \( \psi \)) depending on the centrifugation parameters for an undistributed sample has the following form [13]:

\[
|P| \text{[kPa]} = |\psi| \text{[J/kg]} = - \left( 0.011 \cdot n^2 \cos(\alpha) + g \cdot h \cdot \sin(\alpha) \right) \cdot h,
\]

where \([N] = \text{rpm}, [R] = \text{m}, \text{ and } [h] = \text{m}, |P|, |\psi| \) are absolute values as the water pressure and potential in porous media have negative sign by definition.

Experimental WRC data were approximated using the van Genuchten [11] model, which relates the variable values of pressure (\( P \)) and soil moisture (\( W \)) by the following nonlinear relationship:

\[
W = W_r + \frac{(W_s - W_r)}{\left(1 + (\alpha P)^m\right)^n},
\]

where \( W_r \) - residual moisture, corresponding to almost a fixed tightly bound moisture, \( W_s \) - moisture in a state of saturation of the soil (full water capacity), \( \alpha, n, m \) - empirical constants, and \( m = 1 - 1/n \). To estimate the parameters \( W_r, W_s, \alpha, n \) according to experimental data for WRC as a sequence of \( W(P) \) was used the program S-Plot, version 7, which allows to solve the problem of non-linear regression by iteration method through the built-in least squares algorithm (Regression Wizard).

3. Results of study
The WRC of sandy substrate had a characteristic shape, as was shown by the analysis of experimental results (Figures 1; 2, control) and known literature data [11, 14, 15]. Weak energy of retention in coarse media with large pores caused an almost complete drainage in a very narrow range of water suction (about 10 kPa). At higher suctions, the angle of the WRC increases steeply, since the water remaining in few fine pores at the bridges between coarse particles and sorbed water are retained proportionally to the preparation rate in a whole range of absolute soil water potentials from 0 to 3030 J/kg (Figures 1; 2). The FWC value in the presence of the SSPH (0.2 –0.3 %) exceeded 18–25% depending on the differences in degree of free swelling. This is easy to explain if we take into account that SSPH never reached their maximal swelling capacity in pore space [9]. At water saturation level of the sand-gel composition (\( W_s = 40-50\% \)) the SSPH degree of swelling as ratio “Ws/dose” will be equal to 100-500 gH\(_2\)O/g or less than the maximal degree of free swelling, which can reach 700-1000 gH\(_2\)O/g for Aquasorb super absorber. This circumstance allows to produce agriculture products less expensive and more resistant to unfavourable soil factors like new Russian preparations filled by humates or peat and mineral components with medium degree of swelling [9]. Inclusion of ionic groups of electrolytes in the acrylates and humates form in the structure of a polymer matrix allows to solve the problem of reducing the SSPH swelling as affected by osmotic stress [1]. In this case, embedded cations can exchange ions and serve as a source of elements of plants mineral nutrition. As shows the experiment with SSPH, swelling in a solution of ionic silver, the composition based on it did not worsen much the
water retention properties, which remained at the frames of standard deviations of studied WRC. Only high dose of Aquasorb SSPH (0.3%) at maximal concentration of Ag⁺ (100 mg/l) significantly lost swelling capacity at whole diapason of water retention energy (Figure 1-C). The SSPH at the more effective, from the economical point of view, doses 0.05-0.1% were resistant to osmotic stress. This allows us to recommend a simple technological way of injecting water-soluble plant protection products and eliciting admixtures directly into the matrix solution while preparing gel compositions from dry preparations before these compositions enter the soil. We can assume that as well for the hydrophobic agents, being used in crop production as fungicides and antimicrobials, such mechanical embedding in gel compositions on basis of peat and their following strengthening will be successful owing to amphiphilic polymer structure.

Table 1. Parameters of WRC approximation by van Genuchten model (3)

| SSPH rates and solutions: | Wᵣ | n | α | Wᵣ | R² | s |
|--------------------------|-----|---|---|-----|----|---|
| Monomineral quartz sand (control) | 22.7±0.7 | 2.25±0.20 | 0.32±0.05 | 1.33±0.30 | 0.996 | 0.68 |
| 0% | 32.9±1.8 | 2.10±0.31 | 0.18±0.04 | 3.97±0.84 | 0.981 | 1.74 |
| Hydrophilic Aquasorb SSPH (Germany). | 38.7±1.7 | 1.68±0.16 | 0.14±0.04 | 4.84±1.28 | 0.998 | 1.66 |
| 0.05% pure water | 36.4±2.0 | 1.98±0.90 | 0.15±0.04 | 4.89±1.10 | 0.973 | 2.07 |
| 0.1%+Ag⁺10mg/l | 38.6±1.1 | 1.87±0.13 | 0.16±0.02 | 4.23±0.66 | 0.994 | 1.13 |
| 0.1%+Ag⁺100mg/l | 49.2±2.5 | 1.40±0.13 | 0.21±0.10 | 3.79±2.05 | 0.984 | 2.36 |
| 0.2% pure water | 45.7±2.0 | 1.50±0.13 | 0.21±0.07 | 5.52±2.15 | 0.988 | 1.87 |
| 0.2%+Ag⁺10mg/l | 44.3±2.6 | 1.38±0.14 | 0.25±0.16 | - | 0.973 | 2.36 |
| 0.2%+Ag⁺100mg/l | 47.3±1.8 | 1.37±0.10 | 0.27±0.10 | 4.33±3.03 | 0.990 | 1.65 |
| 0.3% pure water | 48.6±2.4 | 1.30±0.13 | 0.18±0.10 | 1.42±0.83 | 0.992 | 2.25 |
| 0.3%+Ag⁺10mg/l | 48.6±0.6 | 1.39±0.03 | 0.42±0.05 | 3.07±0.79 | 0.999 | 0.50 |
| 0.3%+Ag⁺100mg/l | 33.4±0.93 | 1.77±0.13 | 0.06±0.01 | 2.23±0.89 | 0.995 | 1.08 |
| Amphiphilic SSPH with a peat filler (Russia) | 37.1±2.3 | 1.81±0.30 | 0.18±0.07 | 5.84±1.37 | 0.973 | 2.22 |
| 0.1% pure water | 35.3±2.2 | 1.83±0.28 | 0.15±0.05 | 5.04±1.33 | 0.976 | 2.16 |
| 0.1%+Ag⁺10mg/l | 37.3±2.0 | 1.82±0.24 | 0.14±0.04 | 4.78±1.29 | 0.982 | 2.04 |
| 0.1%+Ag⁺100mg/l | 40.7±2.3 | 1.67±0.22 | 0.13±0.05 | 5.60±1.93 | 0.979 | 2.33 |
| 0.2% pure water | 39.6±2.0 | 1.50±0.17 | 0.19±0.08 | 5.77±2.30 | 0.973 | 1.96 |
| 0.2%+Ag⁺10mg/l | 38.6±1.5 | 2.00±0.22 | 0.11±0.02 | 7.00±0.83 | 0.990 | 1.52 |
| 0.2%+Ag⁺100mg/l | 51.9±2.56 | 1.49±0.16 | 0.21±0.09 | 7.74±2.88 | 0.983 | 2.43 |
| 0.3% pure water | 48.1±2.4 | 1.31±0.13 | 0.23±0.12 | 7.77±3.79 | 0.984 | 2.19 |
| 0.3%+Ag⁺10mg/l | 48.9±2.8 | 1.28±0.14 | 0.20±0.12 | - | 0.989 | 2.60 |

- no significant differences from zero
At the end of the paper, we briefly touch on the mathematical simulation of WRC for soil substrate under the impact of SSPH. Almost all the WRC was adequately described by the van-Genuchten function with the nonlinear regression coefficients $R^2 \geq 0.97-0.99$, estimation parameters $\alpha$ and $m$ ($n$) statistically significant at the probability level of $p \leq 0.001$, and standard errors not exceeding confidence intervals of variation of the $P(W)$ dependences studied (Table 1). All the curves in Figures 1; 2 represent the results of experimental data approximation by the van-Genuchten equation (3). Reliable approximation results by the van-Genuchten equation allow us to use the computer models of HYDRUS-type [10] in the future where it is the standard function to forecast the dynamics of water consumption and plants productivity under the SSPH effect.

Summarizing the results of assessing the water retention capacity we can conclude that a significant increase in the water retention capacity was revealed for the mineral light-textured soil substrate, which corresponded to the heaving of the soil texture by 1–2 gradation levels at SSPH rates of 0.05–0.3%. The highest effect is observed for the nonsaline samples (pure water), however incorporation 10-100 mg/l ionic silver into the soil solution leads to not significant decreasing of water retention of the 0.05-0.1% SSPH compositions. It allows us to inject soil-gel compositions 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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References
[1] Kazanskii K S, Rakova G V, and Enikolopov N S 1986 Strongly swelling polymer hydrogels as water-retaining soil amendments, in Natural Resources of Deserts and Their Development, Ashkhabad, Ylum 147-148 [in Russian]
[2] Al-Darby A M, Al-Asfoor S I, and El-Shafei Y Z 2002 Effect of Soil Gel-Conditioner on the Hydrophysical Properties Sandy Soil J. Saudi Soc. for Agric. Sci. 1(1) 14-40.
[3] Smagin A V and Sadovnikova N B 1994 Impact of Strongly Swelling Hydrogels on Water-Holding Capacity of Light-Textured Soils Eur. Soil Sci. 27 (12) 26–34
[4] Smagin A V and Sadovnikova N B 2015 Creation of Soil-Like Constructions Eur. Soil Sci. 48 (9) 981–990 doi10.1134/S1064229315090100
[5] Raju M P and Raju K M 2001 Design and synthesis of superabsorbent polymers J. of Appl. Polymer Sci. 80(14) 2635–39
[6] Wu L and Liu M 2008 Preparation and characterization of cellulose acetate-coated compound fertilizer with controlled-release and water-retention Polymers for Advanced Technologies 19(7) 785–792
[7] Demitri C, Scalera F, Madaghiele M, Sannino A, and Maffezzoli A 2013 Potential of Cellulose-Based Superabsorbent Hydrogels as Water Reservoir in Agriculture International J. of Polymer Science 2013 Article ID 435073, 6 pages, http://dx.doi.org/10.1155/2013/435073
[8] Narjary B, Aggarwal P, Kumar S, and Meena M D 2013 Significance of Hydrogel and its application in agriculture Indian Farming 62(10) 15-17
[9] Smagin A V, Sadovnikova N B, and Nikolaeva E I 2014 Thermodynamic Analysis of the Effect of Strongly Swelling Polymer Hydrogels on the Physical State of Soil and Sediment Samples Eur. Soil Sci. 47(2) 78–88. doi 10.1134/S1064229314020100
[10] Šimůnek J, van Genuchten M T, and Šejna M 2006 The HYDRUS Software Package for Simulating Two- and Three-Dimensional Movement of Water, Heat, and Multiple Solutes in Varibly-Saturated Media. Technical Manual, Version 1.0, PC Progress, Prague, Czech Republic, 241
[11] van Genuchten M T 1980 A closed form equation for predicting the hydraulic conductivity of unsaturated soils Soil Sci. Soc. Am. J. 44 892–898
[12] Budnikov V I, Fedchenko V N, Drobotin D V, Kus’mitsky G E, Sinki V V, Lokotkov A N, Smagin A V, and Nazarov V B 2014 The composite water-holding material and its production method Patent RU №2536509, data 27.12.2014

[13] Smagin A V, Sadovnikova N B and Mizuri Maauia Ben Ali 1998 The Determination of the Primary Hydrophysical Function of Soil by the Centrifuge Method Eur. Soil Sci. 31(11) 1237-44.

[14] Voronin A D 1990 Energy Concept of the Physical State of Soils Eur. Soil Sci. 23(5) 7-19

[15] Dexter A R 2004 Soil physical quality part I. Theory, effects of soil texture, density, and organic matter, and effects on root growth Geoderma 120 201–214.

Figure 1. WRC of mineral-gel compositions under the impact of hydrophilic Aquasorb SSPH (Germany). Doses of SSPH: (A) 0.1%; (B) 0.2%; (C) 0.3%; 1 – control; concentration of Ag+: 2 – 0 mg/l; 3 – 10 mg/l; 4 – 100 mg/l; 5 – small dose of SSPH (0.05%) in pure water.
Figure 2. WRC of mineral-gel compositions under the impact of amphiphilic SSPH with a peat filler (Russia). Doses of SSPH (A) 0.1%; (B) 0.2%; (C) 0.3%; 1 – control; concentration of Ag⁺ 2 – 0 mg/l; 3 – 10 mg/l; 4 – 100 mg/l; 5 – small dose of SSPH (0.05%) in pure water.