Specific surface area of strongly swelling polymer hydrogels for agriculture

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Abstract. The study is the first attempt in soil physics to estimate the effective specific surface area of strongly swelling polymer hydrogels as soil conditioners of a new generation. Along with the standard assessment of water vapor desorption isotherms by the BET method, a new method for determining the specific surface area deduced from the slope of water retention curves was used. Water desorption isotherms and water retention curves were obtained by a dynamic sorption equilibrium method and by a new method of thermodesorption. The specific surface area values of synthetic polymer hydrogels ranged from 468 to 1029 m\textsuperscript{2}/g. An innovative Russian product VM-P with amphiphilic filler in the form of dispersed peat had the maximum specific surface area among all studied types of hydrogels. Water absorption properties and dispersion of gels have a hysteresis caused, presumably, by the dynamics of dispersion in the cycles of wetting-drying.

1. Introduction
The high water-absorbing properties of synthetic gel structures along with their ability to fix mineral fertilizers and plant protection products in the plant rhizosphere [1–8] are largely determined by the dispersion and surface energy of strongly swelling polymer hydrogels (SSPHs). However, until now, in soil science no data on the dispersion of SSHPs were available. Granulometric analysis of such objects with a fuzzy boundary is impossible, and the evaluation of the effective specific surface area ($S$) as an indicator of dispersion is complicated by its potentially high values. According to the [9] manual, the standard Dynamic Dewpoint Method is limited to $S$ values of no more than 500-600 m\textsuperscript{2}/g, above which the accuracy of the estimation drops sharply. The significance of SSPHs dispersion assessment, along with the noted methodological problems, determined the objectives and novelty of this study, viz. the first attempt to assess the effective specific surface area of different types of SSHP using new instrumental methods and approaches.

2. Objects and methods

2.1. Objects (materials)
The studied materials were presented by the following 5 types of granulated with a grain size of 1-3 mm hydrogels [1, 7, 10, 11]:
1. European (France, Germany) "Aquasorb" trade mark with maximal degree of swelling in pure water (700–1000 kg H₂O/kg);
2. Synthesized in Institute of Chemical Physics of the Russian Academy of Science radiation-cross-linked polyacrylamide (PAA) with a water limit swelling index of 700-1000 kg/kg;
3. Patented [10] Russian hydrogel VUM-ITH (Ural chemical factory) synthesized from the base co-polymer of acrylamide and ammonium acrylate filled by solid biocatalytic wastes and filterperlit with a degree of swelling of not more than 400 kg/kg;
4. Patented [10] hydrogel VUM-H as an analogue of VUM-ITH with the same swelling index but filled by amphiphilic additives in the form of humates;
5. Patented [11] hydrogel VM-P synthesized from the base co-polymer of acrylamide and sodium acrylate and containing, as a filler, an amphiphilic finely dispersed peat and ionic silver with maximal degree of swelling not more than 500-700 kg/kg.

2.2. Theoretical approaches
As a standard, the classical Brunauer-Emmett - Teller (BET) approach for calculating the specific surface area by water vapor desorption isotherms (DSIs) of a polydispersed porous system was used [12, 13]. The desorption isotherm was approximated by the BET model in a linear form:

\[ F_{\text{BET}} = \frac{r_h}{W(1-r_h)} = \frac{1}{W_0K} + \frac{(K-1)}{W_0K} \left( \frac{P}{P_0} \right), \quad (1) \]

where \( r_h \) is water activity (air relative humidity), \( W \) is the mass water content (humidity, kg/kg) and \( K \) and \( W_0 \) are model parameters. In the \( x=r_h, y=F_{\text{BET}}=r_h/W(1-r_h) \) coordinates, the model (1) has the form of \( y = mx + n \) i.e. a linear dependence. Approximating experimental DSIs by this dependence and determining approximation parameters \( n \) and \( m \), the required \( S \) value is easily calculated as follows [14, 15]:

\[ S_{\text{BET}} = \frac{W_0s_0N_A}{M} = \frac{36.14}{n + m}, \quad (2) \]

where \( N_A \) is Avogadro’s number, \( s_0 \) is area per adsorbate molecule, \( M \) is a molecular mass of adsorbate and 36.14 is the numerical expression of the combination of all constants in equation (2) for water molecules.

An alternative approach to estimating the effective specific surface area was proposed in [16]. It is based on the fundamental ion-electrostatic model of wedging pressure, which predicts the linear form of water retention curve (WRC) in semi-logarithmic coordinates for a colloid-dispersed system:

\[ \ln|\Psi| = a - bW, \quad (3) \]

where \(|\Psi|\) is the absolute thermodynamic potential of water, \( a, b \) are physically based parameters reflecting the dispersion and surface energy of the colloidal-dispersed complex of the solid phase. Approximation of the data of WRC sorption part by equation (3) allows to estimate the effective specific surface area using the formula [16]:

\[ S_{wrc} = \frac{1}{2bpr}, \quad (4) \]

where \( r = 1.38 \cdot 10^{-10} \) m is a crystallochemical radius of a water molecule, \( \rho[kg/m^3] \) is the water density.

2.3. Instrumental methods of experiments
Water vapor desorption isotherms and WRCs were obtained by two independent methods. The first is a modification of the well-known classical method of adsorption interfacial equilibrium in the "adsorbent-adsorbate" system [12]. Since the standard analysis of isothermal desorption of water vapor by materials in a static atmosphere at room temperature is extremely slow (1 month or more), we proposed a dynamic modification in which the sample was placed in an inert carrier gas (N₂)
current with a given relative humidity ($rh$). For the necessary wetting, the gas carrier barboted the saturated solutions of the following chemically pure salts: $K_2SO_4$ ($rh=0.98$); KCL ($rh=0.86$); $\text{Ca(NO}_3)_2$ with a given relative humidity ($rh$). For the necessary wetting, the gas carrier barboted the saturated solutions of the following chemically pure salts: $K_2SO_4$ ($rh=0.98$); KCL ($rh=0.86$); $\text{Ca(NO}_3)_2$ ($rh=0.55$); $\text{MgCl}_2$-$6\text{H}_2\text{O}$ ($rh=0.33$); LiCl ($rh=0.15$).

The equilibrium state of the "adsorbent-adsorbate" system was controlled by periodic weighing of the samples with subsequent calculation of their water content ($W = m/m_s$, where $m$ is the mass of water, $m_s$ is the mass of the solid phase of the sample obtained by standard drying at 105°C) for small SSPHs samples, equilibrium in such a dynamic system at room temperature is achieved in 2-4 days, that significantly reduces the experiment compared to the classical adsorption-static method. Due to the possible phenomenon of DSIs hysteresis, the initial moistening of SSHPs samples was carried out in two ways. In the first case, the dry gel was exposed for 6 months in the atmosphere of the desiccator with a distilled water at a temperature of 20 °C. In the second way, the same procedure was applied to the hydrogel, pre-swollen in a distilled water to a value of $W=100 \text{ kg/kg}$.

DSIs as functions $W(rh)$ were approximated by BET equation (1) in a linear form with the evaluation of parameters $m, n$, by which $S_{BET}$ values were calculated according to (2). For DSIs transfer to WRCs, the well-known Gibbs thermodynamic ratio was used [17]:

$$\Psi = \frac{RT}{M} \ln(rh),$$

where $R=8.314 \text{ J/(mol-K)}$ is universal gas constant, $T [\text{K}]$ is the absolute temperature in the drying oven, $M = 0.018 \text{ kg/mol}$ is the molar mass of water.

As an alternative, a new express method of water thermodesorption (temperature dehydration) for the analysis of WRCs and specific surface area has been applied, according to our developments [14, 15]. This non-isothermal method uses heating at different temperatures of the drying oven to remove water from the dispersed material in a laboratory room with a constant temperature ($T_r$) and relative humidity ($f$). The thermodynamic potential of water as a function of the drying temperature ($T$) is given by the following fundamental equation [14]:

$$\Psi = Q - pT,$$

where $p = \{Q/T_r - R\ln(f)/M \}$, $Q = 2401 \pm 3 \text{ kJ/kg}$ for the temperature range of 0-100°C is a specific heat of evaporation. KD 200 drying oven (China) with a forced circulation of air was used for differentiated drying of samples at temperature levels 30, 40, 50, 60, 70, 80, 105 °C with a simultaneous control of the relative air humidity and temperature by DS 1923 "hygrochron"
programmed electronic sensors. Figure 1 shows the results of experimental verification of the fundamental formula (6) by an automatic control of temperature and humidity in the drying oven at different temperature levels. As can be seen, the linear trend approximating the experimental data actually coincided with the linear function (6) with the tabulated parameter $Q = 2401$ kJ/kg, which practically confirms the adequacy of the using approach. To assess the water content ($W$), the samples were weighed at each stage of the experiment, (2-3 hours), that guaranteed the achievement of thermodynamic equilibrium for samples with small volumes of about 1 cm$^3$.

**Figure 2.** Water vapor desorption isotherms (main figure) and WRCs (inset) obtained by dynamic desorption. Hydrogels: (A) – Aquasorb; (B) – PAA and VUM-H, (C) – VUM-ITH, (D) – VM-P.
According to the potential Polyani theory [12, 14], the WRC in the sorption part is temperature invariant. This fact gives the possibility to recalculate the WRC into the desorption isotherm at any temperature, using the equation inverse to formula (5):

\[ rh = \exp\{\Psi(W)/RT\} \tag{7} \]

Having known the \( \Psi'(W) \) dependences, function (7) can be used to obtain the isotherms for a standard room temperature \( (T=T_r) \) in the form of the \( W(rh) \) functions [14].

**Figure 3.** Water retention characteristics (A) and water vapor desorption isotherms in BET coordinates (B) obtained for SSPHs by new thermodesorption method [14, 15].

All experiments were performed in triplicate. Approximation of data with a statistical estimation of model parameters was carried out using the application Regression Wizard in the computer program S-Plot 12.
3. Results and discussion

Isotherms of dynamic desorption of water vapor and hydrogels WRCs calculated from them are shown in figure 2. Their analysis shows that SSPHs are highly hygroscopic materials. The maximum hygroscopic water content in equilibrium with water vapor at $r_h=0.98$ reaches 100% (1 kg/kg) and more. This important fact must be considered in the calculation of working doses of SSPHs and in the regulation of prices for such materials depending on humidity (storage and transportation conditions) because in the natural range of humidity variation from 20 to 100%, the commercial mass of SSPHs can vary by 1.5-2 times.

![Figure 4](image_url)

**Figure 4.** Specific surface area of different SSPHs obtained by dynamic desorption (A) and thermodesorption (B) of water vapor. The types of SSPHs: 1a – Aquasorb dry, 1b – Aquasorb wet, 2a – PAA dry, 3a – VUM ITH dry, 3b – VUM-IHT wet, 4a – VUM-H dry, 5a – VM-P dry, 5b – VM-P wet.

Also, interesting is the fact of a very strong DSIs mismatch for dry and pre-swollen SSHPs. Presumably less water absorption capacity in dry gels is caused by a decrease in their dispersion due to coagulation of colloids and conformation of the polymer matrix when reaching critically small distances (near the energy minimum) under the influence of drying. An alternative explanation is the kinetic factor, even in 6 months the thermodynamic equilibrium in desorption of water from swollen gels is not attained. The effect of hysteresis and absorption kinetics in the water absorption process in hydrogels is also indicated by [4].

By the isotherms of desorption of water vapour the WRCs were calculated considering equation (5) (figure 2, inset). All of them are adequately approximated by the fundamental model (3), that confirms the ion-electrostatic mechanism of disjoining pressure in synthetic gel structures. An innovative hydrogel VM-P with amphiphilic filler in the form of dispersed peat had the highest water holding
capacity, followed by the hydrophilic gels Aquasorb, PAA and VUM-ITH. Aquasorb hydrogel with a high water-holding capacity showed minimal differences between the water absorption characteristics for dry and swollen samples, i.e., the minimum hysteresis of DSIs.

Similar dependences were obtained by an alternative method of thermodesorption of water vapor (figure 3-A). In the sequence "VM-P, Aquasorb, VUM-ITH" the hydrogel with amphiphilic filler also had the maximum water absorption capacity. It can be assumed that the reinforcement of the gel structure by amphiphilic fine-dispersed particles causes additional disjoining pressure between the newly formed phase interface surfaces. Since the slope of the WRC in the semi-logarithmic coordinates \( \ln \Psi(W) \), according to equation (4), uniquely determines the specific surface area, a comparison of the curves of the WRCs in figure 3-A indicates an increase in dispersion and surface energy under the influence of the introduction of amphiphilic fine particles into the polymer matrix.

This result is confirmed by the calculation of the specific surface area by two independent approaches – by the WRCs slope in semi-logarithmic coordinates \( \ln \Psi(W) \) and by water vapor desorption isotherms in the BET coordinates (see an example in figure 3-B). A comparative assessment of dispersion magnitudes for all SSPHs is shown in figure 4. The specific surface area of synthetic SSPHs varies in the range of average estimates from 468 to 1029 m\(^2\)/g. Such values of specific surface area are peculiar in nature only for organic matter of the soil, mineral soil colloids and activated sludge [14, 18–20]. These high values are the main reason for the high water retention and absorption capacity of gel structures in soils if they are used as soil conditioners in small (0.1-0.3% by weight) doses. The maximum specific surface area was in pre-swollen SSPHs, the minimum was detected in dry hydrogels, that confirms the thesis [16] about the potential dynamics of soil and soil colloids dispersion in the cycles of moistening-drying. The new VM-P preparation with an amphiphilic filler as well as the hydrophilic Aquasorb hydrogel had the largest effective specific surface area, statistically significantly exceeding 1.5-2 times the \( S \) values in other SSPHs. The differences between the methods of \( S \) evaluation by the standard BET model (1) and by the fundamental ion-electrostatic model (3) were not systematic and were usually within the range of variation of estimates near the mean values. The method of \( S \) estimation by the WRC slope compares favorably with the standard BET method by less variation, as well as by temperature invariance [14].

4. Conclusion
Synthetic SSPHs are highly dispersed physical systems, analogues of soil colloids with an effective specific surface area of 400-1000 m\(^2\)/g. Their water absorption is controlled by the ion-electrostatic mechanism of disjoining pressure, enhanced by the introduction of fine particles with amphiphilic properties into the polymer matrix. WRCs and specific surface area of SSPHs strongly depend on their initial state (dry or swollen gel), which may be due to the potential dynamics of dispersion in the moistening-drying cycles.

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References
[1] Smagin A V and Sadovnikova N B 1994 Impact of Strongly Swelling Hydrogels on Water-Holding Capacity of Light-Textured Soils Eurasian Soil Sci. 27 26–34
[2] Al Darby A M 1996 The hydraulic properties of a sandy soil treated with gel forming soil conditioner Soil Technol. 9 15–28
[3] 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. Agr. Sci. 1 14–40
[4] Bhardwaj A K, Shainberg I, Goldstein D, Warrington D, Levy G J 2007 Water Retention and Hydraulic Conductivity of Cross-Linked Polyacrylamides in Sandy Soils J. Soil Sci. Soc. Am. 71 406–12
[5] Wu L, Liu M and Rui Liang R L 2008 Preparation and properties of a double-coated slow-
release NPK compound fertilizer with superabsorbent and water-retention Bioresource Technol. 99 547–54

[6] Crous J W 2017 Use of hydrogels in the planting of industrial wood plantations Southern Forests: J. Forest Sci. 79 197–13

[7] Smagin A V 2017 Thermodynamic Evaluation of the Impact of Strongly Swelling Polymer Hydrogels with Ionic Silver on the Water Retention Capacity of Sandy Substrate IOP Conf. Series: Earth Environ. Sci. 52 7 (ID 012087)

[8] Smagin A V, Smagina M V, Kolganihina G B, Sadovnikova N B, Gulbe A Y and Bashina A S 2018 Fungicidal and antibacterial activity of the hydrogel compositions with silver Int. J. Eng. Technol. 7 14–20

[9] Moisture Sorption Isotherm Generator 2009 (Operator’s Manual, Version 3.0. Decagon Devices, Inc., 2007–2009 www.decagon.com)

[10] Budnikov V I, Fedchenko V N, Drobinin D V, Kus’mitsky G E, Sinkin 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

[11] Budnikov V I and Smagin A V 2017 Polymer composite moisture-retaining material and method of its production Patent RU №2639789 data 22.12.2017

[12] Gregg J and. Sing K S W 1982 Adsorption, Surface Area, and Porosity (London: Academic press) p 310

[13] Arthur E, Fuller M, Moldrup P and de Jonge L W 2015 Evaluation of theoretical and empirical water vapor sorption isotherm models for soils Water Res. 52 190–205

[14] Smagin A V 2016 Thermogravimetric Determination of Specific Surface Area for Soil Colloids Colloid J. 78 391–396

[15] Smagin A V, Sadovnikova N B, Bashina A S, Kirichenko A V and Vityazev V G 2016 Theoretical and experimental substantiation of a thermogravimetric method for assessing the water-retention capacity and specific surface area of disperse systems Eurasian Soil Sci. 49 1382–91

[16] Smagin A V 2018 About Thermodynamic Theory of Water Retention Capacity and Dispersity of Soils Eurasian Soil Sci. 51 782–96

[17] Voronin A D 1990 Energy Concept of the Physical State of Soils Eurasian Soil Sci. 23 7-19

[18] Smith P G and Coakly P 1983 A method for determining specific surface area of activated sludge by dye adsorption Water Res. 17 595-98

[19] Andreadakis A D 1993 Physical and chemical properties of activated sludge floc Water Res. 27 1707-14

[20] Advances in Water Resources & Hydraulic Engineering 2009 (Tsinghua: Univ. Press) p 284