Saturated and unsaturated hydraulic conductivity of synthetic gel structures in coarse textured soil substrates

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Abstract. Saturated and unsaturated hydraulic conductivity as a function of a thermodynamic potential (pressure) of soil water $K(P)$ are investigated in the sandy samples with admixtures of strongly swelling polymer hydrogels (SSPHs) in a wide concentration range from 0.01 to 0.3 %SSPHs. The author’s original centrifugation method has been used along with a kinetic model of the water removal process, which enables to determine the function of water conductivity of gel compositions operating in an unsteady state. In saturation state and within the range of low absolute values of soil water pressure $|P| = 0.3$–20 kPa the SSPHs significantly (2–10 up to 50 times) reduced the hydraulic conductivity in proportion to the dose of a superabsorbent. A heterogeneous layered structure with a layer of pure gel or gel composition 0.1–0.3% SSHP reduces the saturated conductivity by 10–80 times. In the range $|P| = 100$–3020 kPa, the $K(P)$ function, on the contrary, strongly increased up to 10–20 times under the action of SSPHs. The calculation of $K(P)$ using the Mualem theory disagrees with our experimental estimation, especially in a range of low water content, where such a calculation strongly (up to 100-1000 times) underestimates the values of $K(P)$.

1. Introduction

Strongly swelling polymer hydrogels (SSPHs), as soil conditioners of a new generation, are being widely used in the modern intensive farming and crop production aiming to optimize water and mineral nutrition of plants, water retention, soil structure and stability [1-11]. Hydrogel’s working doses (0.05-0.3% by weight) are ten or a hundred times lower in comparison with traditional ameliorants used in amounts of 1-10% and more [8, 9, 10]. SSPHs efficiency is generally evaluated by the water-retention capacity indicators – gel swelling index, soil moisture capacity, and soil water potential [1, 4, 6, 8]. At once, the behavior of water in the physical "soil-gel" system and its availability for plants depend not only on the water-retention capacity, but on the hydraulic conductivity of the porous medium as well. The practical significance of the study is determined by the information support of technologies to optimize the physical properties and anti-pathogenic protection of the rhizosphere using gel structures [11]. Specifically, information on hydraulic conductivity is necessary to predict the risks of removal from the soil of plant protection products and trace elements fixed in the gel structures of the rhizosphere.
However, such full data is available only in rare cases [1, 3]. If soil water motion in an infiltration mode can be investigated effortlessly both in field and laboratory experiments, then derivation of the unsaturated hydraulic conductivity function of a porous medium with gel structures presents a certain methodological difficulty. Traditional methods of using capillarimeters, tensiostats, and membrane presses with porous plates are not suitable for this purpose because of colmation of membrane filters with particles of the swollen hydrogel [2]. Moreover, capillarimetric facilities and tensiostats work in a relatively small range of capillary pressure, up to 100 kPa. In our opinion, the most suitable method here is an equilibrium centrifugation that does not require any membranes for separating water from soil-solid matrix [12-14]. All these before-mentioned problems have defined a goal of the present study: by using a centrifugation method to obtain the experimental information concerning the hydraulic conductivity function for coarse textured porous media under the influence of different types of SSHPs in a wide range of absolute values of soil water pressure from 0 to 3030 kPa.

2. Objects and methods
As strongly swelling polymer hydrogels, we tested the radiation-cross-linked technical polyacrylamide (PAA), synthesized in Institute of Chemical Physics of the Russian Academy of Science. This gel has a water limit swelling index of 700-1000 kg/kg [8]. We also tested an innovative (author’s patent [15]) product of the Ural chemical factory (Russia), VM-P with the co-polymer of acrylamide and sodium acrylate with medium degree of swelling (500-700 kg H2O/kg) containing as a filler (23.5%) a finely dispersed peat and in separate SSHP type 1% additives of ionic silver as a plant protection product. Unlike the hydrophilic PAA, VM-P had amphiphilic properties due to the particles of peat. A mineral coarse textured soil substrate was represented by a medium-grained quartz sand (sample 1) and silty-sandy arenosol from Dubai (sample 2), collected at the Jumeirah Beach (25°13'03.5"N 55°15'25.1"E), UAE. Table 1 contains the basic physical and physico-chemical properties of these substrates.

| Sample | C_{org}, % | Granulometric fractions, mm | S_{c}, m^2/g | γ_{wb}, g/cm^3 | γ_{rb}, g/cm^3 | EC^d, dSm/m |
|--------|------------|-----------------------------|--------------|-------------|-------------|-------------|
| 1      | 0.3        | >0.25                      | 0.25–0.05    | 0.05–0.01   | 0.01–0.005  | 0.005–0.001 | 3.9        | 12.1        | 1.43        | 2.61        | 4.6         |
| 2      | 0.1        | 0.25–0.05                  | 0.05–0.01    | 0.01–0.005  | 0.005–0.001 | <0.001      | 1.7        | 0.6         | 0.9         | 5.3         | 12.9        | 1.63        | 2.65        | 0.3         |

^a specific surface area (BET estimation on the desorption of water)
^b bulk density of soil
^c density of soil solid phase
^d electrical conductivity of a soil paste

The gel compositions contained from 0.1 to 0.3% SSHPs by dry weight of the mineral substrates and were prepared by mechanical blending of the pre-calculated amount of hydrogels, preliminarily swollen in distilled water, with sandy substrates. Such method, unlike a dry blending, guaranteed a uniform distribution of small SSHPs doses in the mineral substrate.

Saturated hydraulic conductivity was determined at the laboratory permeameter [2, 16] in cylindrical columns 10 cm long with water supply to the surface of the sample by a Mariott device in the automatic mode of non-pressure flow. To evaluate the hydraulic conductivity function of samples in the unsaturated state, the author’s original centrifugation method was implemented. The method is based on utilization of 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) [13]. As shown in [14], almost the same method of centrifugation is in a good agreement with the standard porous plate method and the discrepancy between them does not exceed 2% of the average variation with a standard deviation of 2.2%. In contrast to works [12, 14], our method...
estimates the hydraulic conductivity in a transient regime using kinetic curves of sample’s drainage. To obtain them, at each step of centrifugation with an assigned rotation speed, a sample is weighed for several (3-4) times as far as it achieves a balance between water removing and restraining forces. Based on the results of weighing, we determine a dependence of sample’s water content (W) on time (t). Approximation of kinetic curves of moisture removal W(t) with an exponential relaxation model (1) allows us to estimate the kinetic constant (k) of the process for each stage of the experiment at a constant rotation speed [13]:

\[ W(t) = W_e + (W_0 - W_e) \exp(-kt). \]  

(1)

Then, the k value is used to calculate the sought quantity of hydraulic conductivity according to [13]:

\[ K = \frac{k(W_0 - W_e) h^2 \rho_e}{100 \rho_r (P_0 - P_e)}, \]  

(2)

where \(W_0, W_e,\) and \(P_0, P_e\) are initial and equilibrium water content (per weight) and absolute pressure of soil water at a given centrifugation step, \(h\) is the height of a sample, \(\rho_e\) is the density of water.

Dimensions of physical parameters in (2) are [P] = cm wc, [h] cm, [k] day^{-1}, [K] cm/day. Pressure (potential) of soil water is determined by centrifuge rotation speed and geometric parameters of its rotor as described in [13]. The pairs of K and P_e values, obtained for each speed (pressure), constitute together the desired dependence of K(P). We simultaneously estimate a water retention curve of a sample as a set of P_e and W_e points, by which, according to [8] method, we calculated the volume distribution (V) of pores by their radii (r). Further, we carry out a theoretical calculation of the sought K(P) function according to Mualem [17]. Approximation of experimental data with model (1) and of WRC with the van Genuchten [18] model was performed in the S-Plot-7 program using nonlinear regression problems by the Regression Wizard Algorithm.

3. Results and discussions

3.1. Saturated hydraulic conductivity

This section analyzes the results of column experiments with a silty-sandy arenosol from Dubai (substrate 1) and gel structures based on radiation crosslinked PAA. As can be seen from table 2, the original silty-sandy substrate had a high level of saturated conductivity (Ks) of 220-230 cm/day at bulk densities about 1.4 g/cm³. The combination of the mineral substrate with a working dose of hydrogel 0.1 % SSHP in the case of a dry gel reduces Ks by 1.4 times (up to 159 cm/day), and if the gel was introduced in a partially swollen state – by 3-3.2 times (up to 72 cm/day). In both cases, the density of the system decreased slightly compared to the original soil. These results are related to homogeneous compositions in which the hydrogel was uniformly mixed with the mineral substrate.

The layered method of placing gel structures can lead to a significant reduction in Ks of coarse porous media [2, 9]. In further experiments, this method was used for compositions with hydrogels. The layered combination "sand/0.1 % SSHP/sand" (3 cm layer of a mixture with 0.1 % dry gel in 10 cm column) originally had a Ks = 158 cm/day, but during the 17 hours of the experiment this value gradually fell to 18.9 cm/day, that is, more than 8 times. Relative to the initial Ks of silty-sandy soil, the resulting drop in the Ks of the layered structure was more than an order of magnitude (12 times). The gradual decrease with time in Ks of layered systems with a dry SSHP is obviously caused by a gradual realization of their swelling and colmation of macropores. Therefore, to reduce filtration, it is more profitable to use initially swollen gels.

The increase in the thickness of the 0.1 % wet gel layer in the middle of the sand column up to 5 cm (half the column length) and compaction (up to 1.54 g/cm³) led to the value of Ks = 2.9 cm/day or 80 times less than in the original sand. A higher concentration of SSHP (0.2 %) in the form of a 1.5 cm layer in the center of the silty-sandy column reduced Ks of the latter by 9.5 times to 24.8 cm/day (table. 2). Finally, another variant of the layered structure, 0.5 cm layer of a pure (100 %) swollen PAA, not mixed with a sandy soil and located in the middle of the column, was not less effective, with minimal mechanical effort in the preparation of the composition. The value of Ks at the final stages of
infiltration after 17 hours decreased here from the initial values of 15-20 cm/day to 5.7 cm/day or 39-40 times relative to $K_s$ of the initial soil substrate. The same high efficiency without compaction had only a fairly complex multilayer system with alternating through the sand layers of 0.1% SSPH (3 cm) and 5% peat (2 cm). Its $K_s$ in the first hour was 12 cm/day, and after 17 hours –5.6 cm/day (table 2). The obtained results indicate a high efficiency of gel structures in $K_s$ reducing of coarse porous media.

| Table 2. Column experiments on water filtration in Dubai’s silty-sand arenosol under the influence of synthetic gel structures. |
|---|---|---|
| Materials and their compositions: | $K_s$, cm/day | $\rho_v$, g/cm$^3$ | TP% |
| Homogeneous mixture: |  |
| silty -sand arenosol | 235.1 | 1.44 | 45.7 |
| silty -sand arenosol | 219.9 | 1.40 | 46.2 |
| 0.1%SSHP dry | 159.0 | 1.31 | 50.0 |
| 0.1%SSHP swollen | 71.8 | 1.38 | 48.5 |
| Heterogeneous layered systems: |  |
| sand/ 0.1%SSHP/sand dry gel | 158.0 | 1.38 | 47.9 |
| sand/ 0.1%SSHP/sand after 17 hrs | 18.9 | 1.47 | 44.5 |
| sand/ 0.1%SSHP/sand compacted | 2.9 | 1.54 | 42.9 |
| sand/ 0.2%SSHP/sand swollen gel | 24.8 | 1.48 | 44.2 |
| sand/ 100%SSHP/sand swollen gel | 5.7 | 1.38 | 47.9 |
| sand/0.1%SSHP/sand/5%peat/sand | 5.6 | 1.44 | 45.6 |

*a the total porosity of the sample (averaged over the entire column volume).

3.2. Unsatuated hydraulic conductivity

Figure 1 shows selected results on the kinetics of centrifugation of silty-sandy samples with PAA, confirming the adequacy of the proposed model (1) for the description of water removing by a centrifugal force. The model parameters were statistically significant at a probability level $p \leq 0.01$ with coefficients of determination $R^2 \geq 0.99-0.99$, and small standard errors of approximation $s = 0.5-0.8$ not exceeding the confidence intervals of varying investigated dependencies $W(t)$. According to the kinetic constants and parameters of the equilibrium water content based on equation (2), hydraulic conductivity values were calculated as a function of soil water pressure for the silty-sandy substrate and its compositions with SSPHs. The graphs and their approximation by the power Campbell [19] model are shown in figure 2. The analysis shows that the presence of the gel has a dual effect on the unsaturated hydraulic conductivity of the mineral sandy substrate. In the range of high soil water content and, consequently, low absolute values of soil moisture pressure $|P|$<10-15 kPa, there is a reduction of hydraulic conductivity up to 2-3 times at low doses SSPH of 0.01-0.05% and up to 10-50 times at higher concentrations of 0.1-0.2% SSPH by weight of dry sand. This is apparently due to the increase in the viscosity of the solution and then to colimation by a swollen gel, as in the case of saturated flow (see paragraph 3.1.). At further draining of the sample (negative pressures of 20-700 kPa), the conductivity values begin, on the contrary, increase in proportion to the dose of the polymer. Obviously, the gel particles, localized in the sand, forming a network of thin water-conducting extra tracks in the structure of coarse-textured substrate with large pores, that cannot conduct the water at this pressure. The formation of thin macropores and mesopores (0.1-10 microns) under the influence of SSPH was confirmed by the analysis of pore size distributions in the gel compositions (figure 2, inset). Maxima of dominant pores on the curves shifts to the left, toward the smaller pores, and the
share of the total pore volume in the structure of the gel compositions also regularly rises with increasing SSPHs doses. Hence, soils, conditioned by SSPHs, should have an increased hydraulic conductivity in the area of capillary and film moisture ($|P|>10\text{-}30$ kPa) compared to the control sandy substrates, that is actually observed (figure 1).

\begin{align*}
\text{Figure 1. Kinetic curves of water removal from the soil by a centrifuge and their approximation by model (1). Conventions and approximation equation:} \\
1. & \text{control, 6000 rpm; } W=0.37+(2.94-0.37)\exp(-0.16t); R^2=0.98; s=0.15; \\
2. & 0.01\%\text{SSPH, 3000 rpm; } W=3.88+(9.49-3.88)\exp(-0.31t); R^2=0.99; s=0.37; \\
3. & 0.2\%\text{SSPH, 4500 rpm; } W=8.82+(13.25-8.82)\exp(-0.14t); R^2=0.99; s=0.20; \\
4. & 0.05\%\text{SSPH, 2000 rpm; } W=8.94+(11.79-8.94)\exp(-0.50t); R^2=0.99; s=0.03; \\
5. & 0.05\%\text{SSPH, 3000 rpm; } W=6.70+(11.13-6.70)\exp(-0.35t); R^2=0.98; s=0.26; \\
6. & 0.05\%\text{SSPH, 4500 rpm; } W=4.42+(6.70-4.42)\exp(-0.14t); R^2=0.99; s=0.04; \\
7. & 0.03\%\text{SSPH, 3000 rpm; } W=5.00+(10.89-5.00)\exp(-0.35t); R^2=0.99; s=0.36; \\
8. & 0.2\%\text{SSPH, 2000 rpm; } W=16.33+(19.35-16.33)\exp(-0.50t); R^2=0.99; s=0.07; \\
9. & 0.2\%\text{SSPH, 6000 rpm; } W=4.13+(12.96-4.13)\exp(-0.10t); R^2=0.99; s=0.25.
\end{align*}

A similar dependence of $K(P)$ was obtained in the case of compositions with amphiphilic preparation VM-P in a wider range of variation of absolute values of soil water pressure 0.8-3030 kPa (Figure 3). As well as in hydrophilic PAA, the crossover zone close to 10 kPa was clearly distinguished on the $K(P)$ graphs. Here the water conductivities of the initial substrate and gel compositions became close in values. At higher absolute values of pressure, gel structures explicitly increased hydraulic conductivity in comparison with the initial sandy substrate proportional to the concentrations of SSHP. The greatest effect arose from a maximum dose of 0.3\%SSHP. The physical mechanism of increasing
hydraulic conductivity, as in the previous case, we associate with a change in the pore space of the coarse substrate under the influence of gel structures (figure 3, inset). The presence of silver in the polymer matrix slightly reduced the effectiveness of the maximum dose of 0.3%SSHP. In such samples, hydraulic conductivity and pore distribution became closer to the characteristics of gel structures with a lower dose of 0.2%SSHP.

**Figure 2.** Hydraulic conductivity functions (main figure) and pore distributions (inset) of silty sandy soil substrate under the influence of PAA SSPH and approximation $K(P)$ by Campbell's model.

The power Campbell function [19], suitable for unsaturated flows, is an excellent approximation of the actual data throughout the entire range of $K(P)$ variation, with determination coefficients of $R^2 = 0.98-0.99$ and statistically significant parameters of the approximation, that gradually reduces their values with increasing doses of polymers (figure 3, 4). Simultaneously, most of the modern computer models of soil water motion evaluate the hydraulic conductivity function indirectly from $K_s$ and the WRC, by the help of theoretical equations, for example, the Mualem [1976] function. Figure 4 shows to what extent the calculation method meets the reality for coarse dispersed soil objects. As can be seen, both for the reference sample (silty-sandy substrate) and for its compositions with a hydrogel
(SSPH dose = 0.2%), only in the area close to saturation ($|P| = 0.1-10$ kPa), the correspondence between the calculated and experimental values is observed. With absolute pressure increased, the Mualem method gives a sharp decline of hydraulic conductivity in the sandy substrate, and the differences with the experimental data reach three to four orders of magnitude in the pressure range of 100-1000 kPa. For compositions with hydrogel (0.2% SSPH) having a water retention capacity close to loam, the difference is a bit smaller, and, within the general range of capillary and gravity moisture transfer from 0 to 100 kPa of absolute moisture pressure (potentials) values can be neglected.

**Figure 3.** Hydraulic conductivity functions (main figure) and pore distributions (inset) of a medium-grained sandy substrate under the influence of VM-P SSHP and approximation $K(P)$ by Campbell's model. 1 – mineral substrate (control), 2 - 0.05% SSHP, 3 - 0.1% SSHP, 4 - 0.2% SSHP, 5-0.3% SSHP, 6 - 0.3% SSHP + 1%Ag.
Figure 4. Comparison of Mualem's function (calculation from WRC) and experimental data on the unsaturated hydraulic conductivity: A – control (sand); B – 0.2% SSPH.

However, under stronger drainage within the range of 100-1000 kPa for tested composition, a sharp decrease of the calculated hydraulic conductivity, down to the values of the order of $10^6$ cm/day, is noted, while the experimental data is of the order of $10^3$ cm/day, i.e., thousandfold differences are observed again.

The obtained differences argue a serious problem on the adequacy of evaluation of hydraulic conductivity function in the modern computer models moisture motion regarding the coarse soil and their compositions with SSPHs. Apparently, this is one of the possible reasons for the subsequent discrepancies in the predicted and actual trends in soil moisture dynamics, that are so frequent for computer simulations without prior adjustment (essentially, fitting) of the models.

4. Conclusion

Synthetic gel structures in coarse textured soils strongly (up to 10-100 times) change the saturated conductivity; the greatest effect is achieved by a layered arrangement of gel compositions. The decrease of water permeability in gel structures is a reliable factor for fixing of water-soluble plant protection products in the rhizosphere and preventing their removal from the soil. Unsaturated hydraulic conductivity of sandy soils changes not uniquely under the influence of hydrogels, decreasing up to 10-50 times in the field of low absolute soil water pressure values (0.3-20 kPa) and increasing up to 10-20 times at dryness of 200-3030 kPa. In drought conditions, this can be an important mechanism to increase the resistance of the plant rhizosphere to water stress. The standard calculation according to the Mualem theory strongly (by 2-3 orders of magnitude) underestimates the hydraulic conductivity of a coarse porous media with gel structures, so it is better to use the experimental determination of $K(P)$ for modeling of water transport in these physical systems.

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