ISSN 1064-2293, Eurasian Soil Science, 2014, Vol. 47, No. 6, pp. 591–597. © Pleiades Publishing, Ltd., 2014.
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SOIL PHYSICS

Biodestruction of Strongly Swelling Polymer Hydrogels and Its Effect on the Water Retention Capacity of Soils

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Received September 18, 2013

Abstract—The biodestruction of strongly swelling polymer hydrogels (water adsorbing soil conditioners of the new generation) has been studied at the quantitative level using original mathematical models. In laboratory experiments, a relationship between the hydrogel degradation rate and the temperature has been obtained, and the effect of the biodestruction on the water retention curve of soil compositions with hydrogels (used as an index of their water retention capacity) has been assessed. From the automatic monitoring data of the temperature regime of soils, the potential biodestruction of hydrogels has been predicted for different climatic conditions. The loss of hydrogels during three months of the vegetation period because of destruction can exceed 30% of their initial content in irrigated agriculture under arid climatic conditions and more than 10% under humid climatic conditions. Thus, the biodestruction of hydrogels is one of the most important factors decreasing their efficiency under actual soil conditions.

Keywords: temperature, simulation, water retention capacity, water retention curve

DOI: 10.1134/S1064229314060088

INTRODUCTION

Strongly swelling polymer gels (SSPHs) are actively used in irrigated farming, landscaping, and floriculture for increasing the water retention capacity and regulating the water status of soils and sediments predominantly of light texture [1, 5, 8, 9, 12, 15, 16]. At the same time, some factors of natural soil environments can negatively affect SSPHs and decrease their efficiency as water superadsorbents: the reduced swelling of SSPHs in the rigid pore space of sandy soils and under the impact of the osmotic pressure of soil solution or irrigation water containing soluble salts; the aging of hydrogels (syneresis); and, finally, their destruction under the effect of soil microorganisms. The latter factor is almost unstudied at the quantitative level, although theoretically it can be of significant importance. From the structural formulas of acrylic acid and polyacrylamide (monomers of most SSPHs), hydrogels contain about 50 wt % carbon and up to 19 wt % nitrogen. SSPHs actively sorb water and are enriched with carbon and nitrogen at a rate of C : N = 2.5–2.6; therefore, one may expect the intense destruction of these substances, especially under an arid climate with high soil temperatures. The temperature determines the rate of biodestruction under the optimum moisture conditions for the growth of microflora maintained by irrigation farming technologies.

Therefore, the aim of this work was to study the degradation of SSPH depending on the temperature and to simulate this process for predicting the potential hydrogel loss under different soil–climatic conditions. The effect of biodestruction on the water retention curve (WRC) of soil compositions with SSPHs (selected as a thermodynamic parameter of their water retention capacity) was simultaneously studied in biodestruction experiments, where the losses in water retention because of the degradation of SSPHs can be directly determined for different initial hydrogel rates under different incubation temperatures.

OBJECTS AND METHODS

Laboratory experiments were carried out with samples of monomineral quartz sand and polymineral sandy soil from the Repetek Biosphere Reserve in Kara Kum (physical clay, 5–6%; specific surface for water sorption, 2–3 m^2/g; natural bulk density, 1.5–1.6 g/cm^3; solid phase density, 2.57–2.62 g/cm^3; paste electric conductivity, 1.6–2.2 dS/m). A radiation-grafted technical polyacrylamide with a degree of swelling in water of 700–1000 g H_2O/g synthesized at the Institute of Chemical Physics (ICP) of the Russian Academy of Sciences was used as the SSPH; its concentrations in 0.01–0.1 salt solutions were no lower than 250 g/g [5].

A five-month-long incubation experiment was performed for assessing the biodestruction rate of the SSPH and the decrease in its efficiency. Samples of quartz sand and polymineral sandy desert soil from Kara Kum containing the hydrogel at rates of 0.05, 0.1, and 0.2 wt % of the containing material were exposed in thermostats at constant temperatures of 20, 30, and 37°C, which simulated different biodestruction conditions in the humid and arid climatic zones. The water content of the samples was maintained optimum for destruction at the level of the field capacity and was 10 to 20% depending on the SSPH rate. Before the beginning of the experiment and after its completion, the content of organic carbon and WRT were determined for the samples. The carbon was determined by the Nikitin modification of the classical Tyurin method with photocolorimetric detection [2]. The WRC was assessed using our modification of the equilibrium centrifugation method [8, 10, 13]. The distribution of the pore sizes was calculated from the WRC approximated by the van Genuchten function according to the described procedure [8]. The soil energy constants were analyzed using the Voronin secant method [3] using computer algorithms for searching for the points of intersection with the WRC developed earlier [8]. For the determination of the permanent wilting point from the WRC, the critical water pressure equal to 1500 kPa (absolute value) was taken according to Shein [14].

Automatic monitoring of the air and soil temperatures was performed under arid (city of Doha, Qatar) and humid (city of Moscow) climatic field conditions using a DS 1921 programmable electronic sensor [6]. The statistical and mathematical processing of the data was performed using Microsoft Office Excel 2003 and S-plot 7. The numerical simulation of the SSPH destruction kinetics depending on the temperature conditions was performed using Matlab7 using onboard algorithms for the solution of nonlinear differential equations (ODE 15s) [4].

RESULTS OF STUDIES

In the first experiment, fine quartz sand and its compositions with 0.05, 0.1, and 0.2% SSPH were studied. The addition of hydrogel expectedly increased the water retention capacity of the mineral substrate (Fig. 1). The equilibrium water contents and the values of the total water capacity (TWC) and capillary water capacity (CWC) regularly increased with the increasing SSPH rate. The corresponding TWC and CWC values were 26.2 and 23.8% of the solid phase weight for the control, 32.1–29.5% at 0.05% SSPH, 37.2–33.7% at 0.1% SSPH, and 42.7–38.5% at 0.2% SSPH. Thus, the water capacity increased in this range by 1.4–1.7 times at 0.1–0.2% SSPH. The addition of SSPH for increasing the values of the FC and maximum molecular capacity (MMC) was also efficient. These values varied in the range of 8.7–10.3% in the control and increased to 10.4–12.5% at 0.05 SSPH, 12.4–15.3% at 0.1% SSPH, and 19.4–24.2% at 0.2% SSPH. Thus, the SSPH rates of 0.1–0.2% increased the water capacity of the substrate by 1.5–2.2 times in the region of capillary and film moisture and brought it to the values typical for natural loamy sandy and loamy soils.

The experiment confirmed the conclusion about the availability of water accumulated by the SSPH to plants, which was drawn in some studies of hydrogels [5, 9, 12]. The value of the wilting point (WP) varied from 1.2 (control) to 4.3 (0.1% SSPH) and 7.6% (0.1% SSPH); therefore, the range of available water (FC–WP) increased from 8.5 to 16.6%, i.e., by almost twice. The changes in the structural organization of the substrate at its mixing with the gel were accompanied by a little decrease in the effective diameter of the dominant pores from 0.05 mm in the control to 0.04 mm (at a rate of 0.1%) and 0.023 mm (at a rate of 0.2%). The insignificant changes in the pore size range are apparently related to its symmetrical extension toward both small diameters (fine macropores, mesopores) corresponding to the increase in the FC and MMC and large macropores reflecting the increase in the water retention capacity and CWC.

Experiments on the incubation of samples with gel for 6 months at 20, 30, and 37°C revealed relatively high variability of the physical state and water retention capacity reflected by the WRC and its derivative water capacity parameters (Fig. 1). The highest biodestruction of the SSPH and the corresponding decrease in the water retention capacity were revealed at the maximum incubation temperature (37°C); the lowest changes were found at the minimum temperature (20°C). The incubation at 30°C occupied an intermediate position. These results were expectable, because the rate of the (bio)chemical processes increases by 2–3 times per every 10°C according to the known Van't Hoff rule. The maximum temperature (37°C) was apparently within the optimum temperature range for the group of SSPH-decomposing microorganisms, because a decrease in the biodestruction rate should otherwise be observed.

Specifying the experimental results, we note that the incubation with all three SSPH concentrations (0.05, 0.1, and 0.2%) at 37°C resulted in similar parameter values of the water retention capacity and structural state, insignificantly differing from the control. The water retention capacity and CWC varied in the range of 25–29%, the MMC and FC varied from 9 to 12%, and the WP varied from 1.4 to 1.8% of the solid phase weight.

The concentration of organic carbon determined by Nikitin's modification of the Tyurin method and the following calculation of the SSPH weight showed that the content of gel in this experimental treatment decreased to 0.036–0.051% at initial SSPH rates of 0.05–0.2% and an incubation temperature of 37°C. According to the exponential model of biodestruction

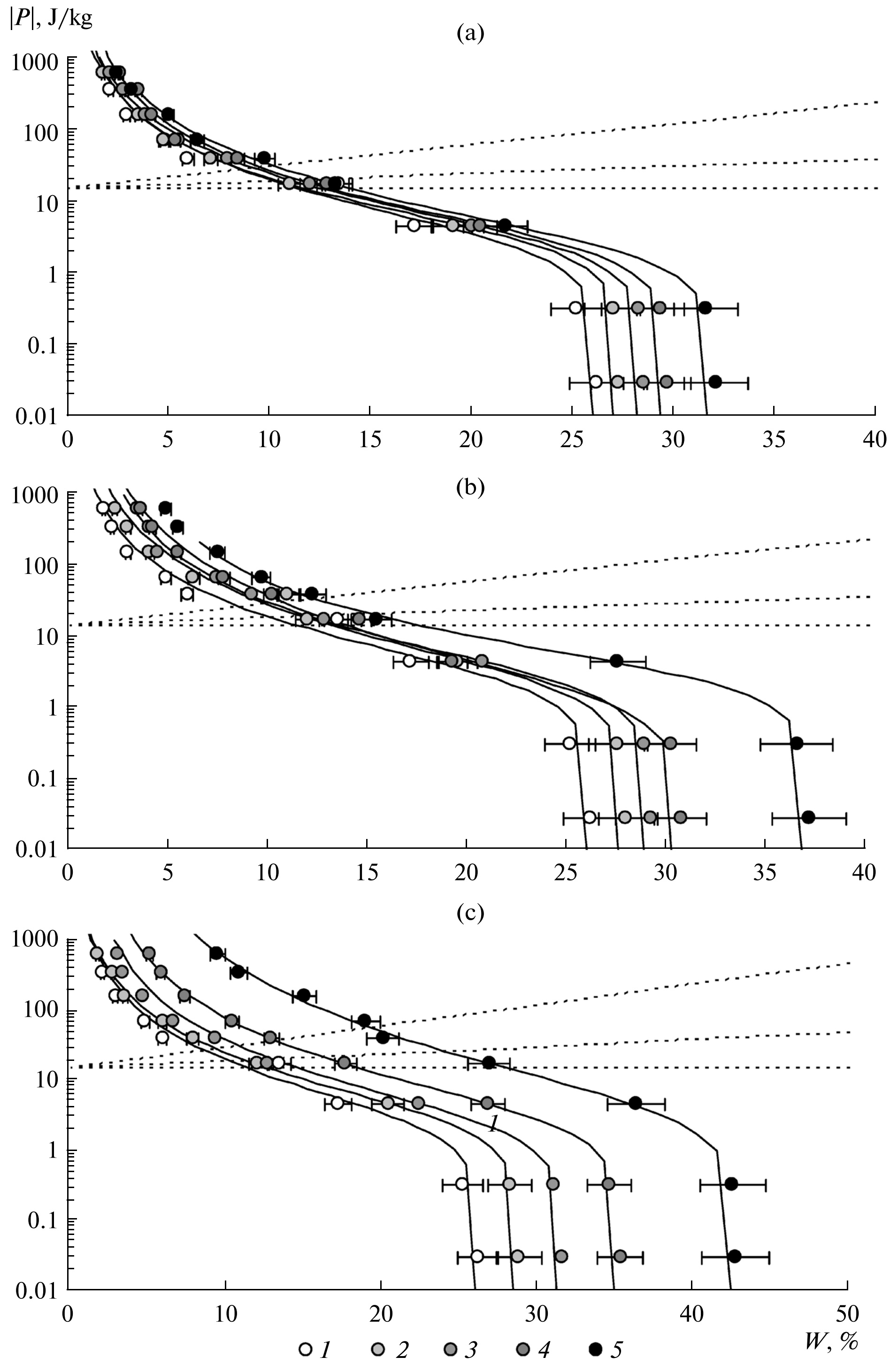

Fig. 1. Dynamics of the monomineral quartz sand WRC under the impact of different rates and biodestruction of the SSPH. The initial hydrogel rate: (a) 0.05%; (b) 0.1%; (c) 0.2%; (*1*) control; (*2, 3, 4*) incubation at 37, 30, and 20°C, respectively; (*5*) initial SSPH rate; (dashed lines) Voronin secants [3]; (curves) data approximations with the van Genuchten model [14].

[8], this destruction rate corresponds to kinetic mineralization constants of 0.7–2.7 year^{-1} or SSPH half-life values of $T_{0.5}$ = 0.4–1.0 years. Almost complete destruction (95% of the SSPH) will be attained at this rate within 1.8–4.3 years according to the parameter $T_{0.95}$ [11]. At this destruction rate, the effect of the SSPH apparently disappears within the first year after its addition in most cases.

A permanent soil temperature of 37°C throughout the year is obviously impossible even under arid cli-

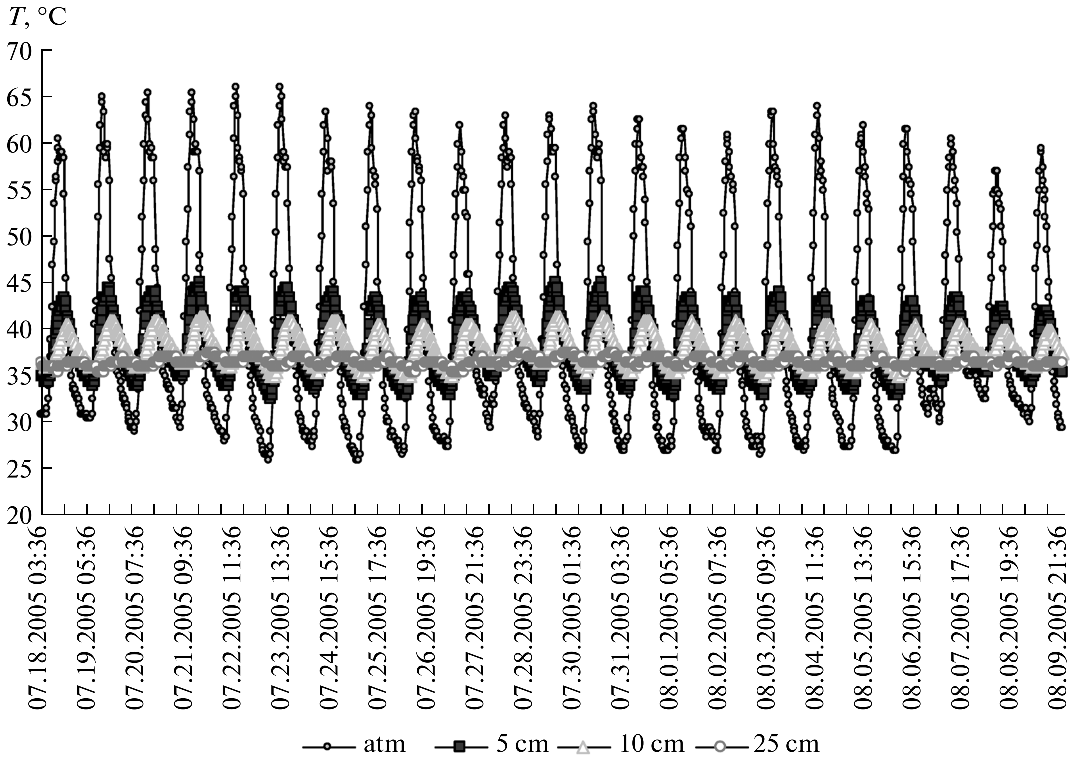

Fig. 2. Automatic monitoring of the soil temperature with DS 1921 thermochron sensors at the Qatar experimental station (a fragment).

matic conditions; however, the revealed biodestruction rate can significantly deteriorate the water retention capacity of soils conditioned with SSPH already within the first two–three months of the hot vegetation season. Our observations of the atmosphere and sandy desert soil temperatures at the experimental station of the Qatar Ministry of Municipal and Agricultural Affairs using programmed DS 1921 thermochron sensors [16] showed that the mean soil temperature in the 0- to 30-cm root-inhabited layer in the summer is about 37–38°C with daily amplitudes of 5–10°C; the atmospheric temperature reaches 40°C (Fig. 2).

The incubation of the samples at 30°C slightly decreased the degradation rate of the SSPH and the soil physical state compared to 37°C. The concentrations of SSPH to the end of the experiment were 0.045–0.086% for the initial rates of 0.05–0.2% SSPH, which corresponded to kinetic mineralization constants of 0.4–1.7 year^{-1}, or the SSPH degradation times $T_{0.5}$ = 0.4–1.7 years and $T_{0.95}$ = 1.7–7.5 years. As a result of the SSPH biodestruction, the TWC and CWC decreased to about 26–33%, the MMC and FC decreased to 9.5–13%, and the WP lowered down to 1.3–2.6% (for the studied range of SSPH rates of 0.05–0.2%).

The highest stability of the SSPH and, hence, its aftereffect were revealed in an experiment at room temperature (about 20°C). The destruction rate of the hydrogel assessed from the exponential model was characterized by constants of 0.2–1.5 year^{-1}, or the SSPH degradation times $T_{0.5}$ = 0.5–3.5 years and $T_{0.95}$ = 2–15 years. The analysis of the WRC revealed higher water capacities in the entire range of variable water content and capillary-sorption potential. Thus, the values of the CWC and TWC varied in the range of 27–35%, the MMC and FC values were in the range of 10–16%, and the WP was 2.8–3.8% after the end of the incubation for the compositions with initial rates of 0.05–0.2% SSPH. As a result, statistically significant differences in the parameters of the water retention capacity from the control by 1.3–1.5 times for the rates of 0.1–0.2% remained to the end of the experiment.

Similar results for the effect of the biodestruction of the SSPH on the physical state of the conditioned coarsely dispersed substrate were obtained with the second series of samples based on polymineral sandy soil from Kara Kum (Fig. 3). It can be seen that the initial water retention parameters of this soil were slightly higher than those of quartz sand, especially in the near-saturation range. The values of the CWC and TWC for this substrate were 34.2 and 40.4%, respectively; the MMC = 9.4%, the FC = 10.9%, and the WP = 4.5%. The addition of similar SSPH rates (0.05, 0.1, and 0.2%) to the wet substrate followed by free swelling resulted in a shift of the WRC to the right against the control, an increase in the potentials and the equilibrium water content, and an adequate shift in the effective diameter of the pores dominating in the

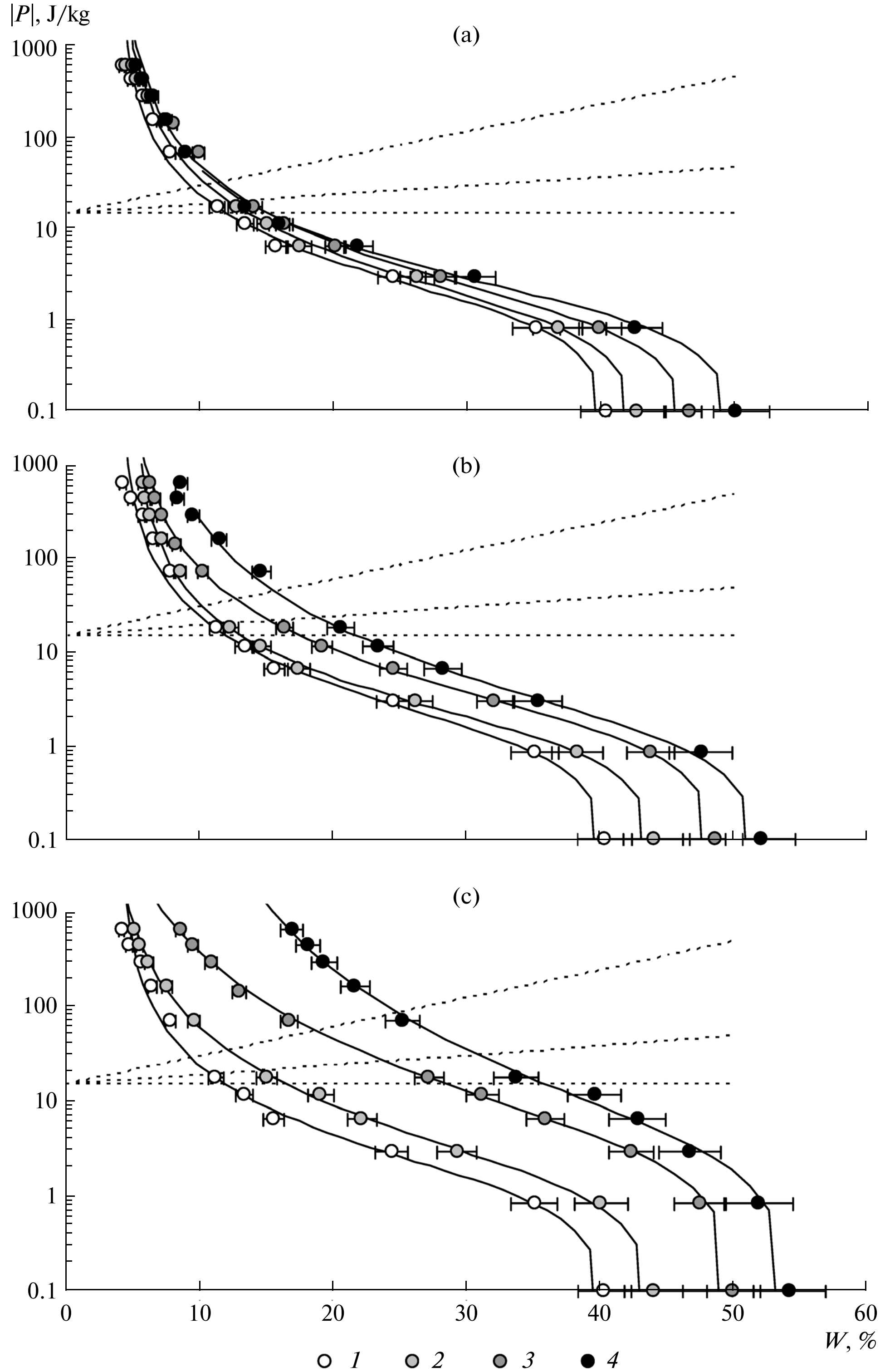

Fig. 3. Dynamics of the polymineral sandy soil WRC under the impact of different rates and biodestruction of the SSPH. The initial hydrogel rate: (a) 0.05%; (b) 0.1%; (c) 0.2%; (*1*) control; (*2, 3*) incubation at 37 and 20°C, respectively; (*4*) initial SSPH rate; (dashed lines) Voronin secants [3]; (curves) data approximations with the van Genuchten model [14].

substrate structure (from 0.13 mm for the control and 0.05% SSPH to 0.09 mm for 0.1% SSPH and 0.03 mm at 0.2% SSPH (Fig. 3)). The low concentration of SSPH (0.05%) appreciably increased the values of the CWC and TWC (to 45–50%) and slightly increased the water retention in the ranges of the capillary and

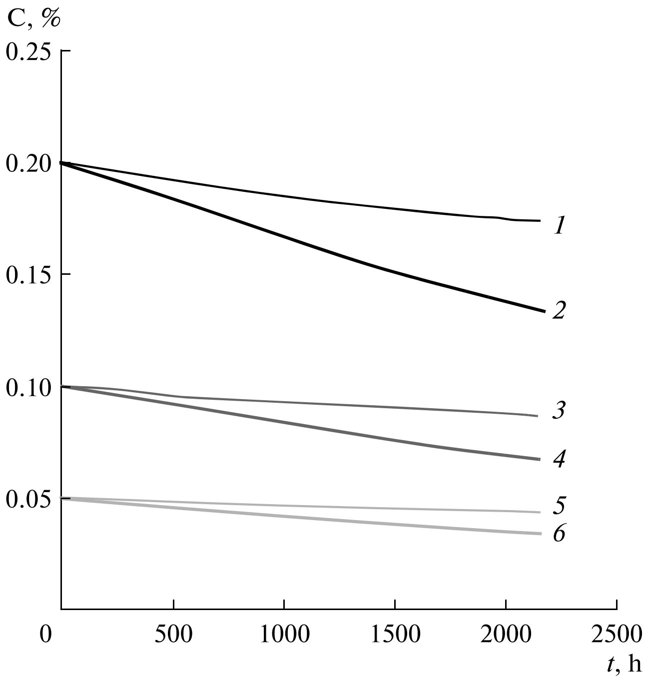

Fig. 4. Numerical simulation of the biodestruction of the SSPH as a function of the temperature: (*1*, *2*) 0.2% SSPH under arid and humid conditions, respectively; (*3*, *4*) 0.1% SSPH under arid and humid conditions, respectively; (*5*, *6*) 0.05% SSPH under arid and humid conditions, respectively.

film water (FC = 13.3%; MMC = 11.2%). The SSPH rates of 0.1–0.2% brought the CWC and TWC to 49–54% and the MMC and FC to 17–31%, i.e., to the values typical for soils with medium and heavy textures. The value of the WP also increased to 7.5–14%; however, the more significant increase in the FC enlarged the available water range from 6% in the control to 11–17% at 0.1–0.2% SSPH.

As far as the destruction of the SSPH proceeded, the primarily reached high parameter values most rapidly decreased at the highest incubation temperature (37°C), as in the above experiment with quartz sand (Figs. 1 and 3). At an SSPH rate of 0.05%, the values of the CWC and TWC decreased to 39 and 43% at 37°C and to 43 and 47% at 20°C, respectively. Almost no differences in the MMC and FC were observed, and both values remained at the initial level of 11–13% obtained for the initial composition with 0.05% SSPH regardless of the incubation temperature.

The incubation at the higher SSPH content (0.1%) at 37°C resulted in a decrease in the TWC to 44%, the CWC to 39%, the FC to 10.8%, and the MMC to 10.2%, whose values approached those of the initial substrate without SSPH. At the lower temperature (20°C), the residual values of the water capacity were higher and varied from 13–15% for the MMC and FC to 45–49% for the CWC and TWC.

The highest aftereffect was revealed at the maximum initial SSPH rate (0.2%). In this case, the CWC and TWC decreased to 41–44%, and the MMC and FC decreased to 12–15% at the incubation temperature of 37°C. The incubation at a lower temperature (20°C) allowed the water capacity parameters to remain at higher levels: 47–50% for the CWC and TWC and 19–24% for the MMC and FC. Thus, the initial almost triple increase in the water retention capacity of the soil, which was characterized by the FC at the addition of 0.2% SSPH after incubation at 20°C, decreased to its double value.

The biodestruction rate of the SSPH, which was also assessed from the initial rate and residual concentration of the gel minus the carbon of the natural organic matter (humus), was characterized by kinetic degradation constants of 0.7–1.7 year^{-1} and degradation times of $T_{0.5}$ = 0.4–1.0 years and $T_{0.95}$ = 1.8–4.3 years for an incubation temperature of 37°C. At a lower temperature (20°C), the destruction decelerated, and the kinetic constants decreased to 0.4–0.7 year^{-1}, which was equivalent to $T_{0.5}$ = 1.0–1.7 years and $T_{0.95}$ = 4.3–7.5 years for all the studied SSPH rates in the range of 0.05–0.2%.

The generalized results of two biodestruction experiments with quartz sand and polymineral sandy soils allowed revealing the temperature (T) dependence of the kinetic degradation constants of the SSPH (k). It had an exponential form and was described by the following equation: $k(T) = 0.2834\exp(0.0435T)$. From the obtained relationship, the potential degradation of the hydrogel was calculated using the modified exponential model of biodestruction:

$$\frac{dC}{dt} = -k(T)C, \quad (1)$$

where C is the content of hydrogel. The temperature was taken as a function of time ($T(t)$ from the actual data obtained under arid and humid climatic conditions [8]. In particular, the data of the experimental station of the Qatar Ministry of Municipal and Agricultural Affairs for the arid zone (Fig. 2) were approximated by the least squares method under S-plot 7 using the following empirical equation: $T(t) = T_0 + a\sin(2 \times 3.14t/b + c)$, where $a = 4.45$, $b = 23.85$, $c = 4.18$, and $T_0 = 38.14$.

Calculations of the destruction rates performed using model (1) under Matlab-7 showed that the potential losses in this treatment make up 9–10% for 580 h (less than a month) and reach 33% of the initial content for three months regardless of the SSPH rate (Fig. 4). The use of temperature data typical for the humid climatic conditions of the capital of the metropolis according to [8] with the spline approximation of the dependence $T(t)$ for an analogous numerical simulation showed that the destruction of the gel proceeds in this case more slowly than in the irrigated arid soils. About 10–13% of the initial SSPH content (rate) is lost during a vegetation season. However, this is also a relatively high rate in technological terms.

Thus, the biodegradation of SSPH as a water-saturated organic substance enriched with carbon and nitrogen is an essential factor decreasing its efficiency under production conditions. Therefore, along with the determination of the technological parameters by simulating the consumption and transport of water and nutrients, the negative consequences for the soil materials and, primarily, their microbial destruction must be considered in projects of soil constructions.

ACKNOWLEDGMENTS

This work was supported in part by the Russian Foundation for Basic Research, project no. 12-04-00528-a.

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Translated by K. Pankratova