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Silanized humic substances act as hydrophobic modifiers of soil separates inducing formation of water-stable aggregates in soils

Alexander B. Volikov [a], Vladimir A. Kholodov [b,c], Natalya A. Kulikova [b,d], Olga I. Philippova [b], Sergey A. Ponomarenko [a,e], Elena V. Lasareva [a], Aksana M. Parfyonova [a], Kirk Hatfield [f], Irina V. Perminova [a,*]

[a] Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory 1–3, 119991 Moscow, Russia
[b] Department of Soil Science, Lomonosov Moscow State University, Leninskie Gory 1–12, 119991 Moscow, Russia
[c] Dokuchaev Soil Science Institute, RAAS, Pyzhevsky Per. 7, 119017 Moscow, Russia
[d] Bach Institute of Biochemistry, RAS, Leninsky Pr. 33, Bldg. 2, 119071 Moscow, Russia
[e] Enikolopov Institute of Synthetic Polymeric Materials, RAS, Profsoyuznaya Str. 70, Moscow 117393, Russia
[f] Engineering School of Sustainable Infrastructure and Environment, University of Florida, Gainesville, FL 32611, USA

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ABSTRACT

In this study we successfully enhanced surface activity of natural humic substances (HS) with respect to mineral surfaces by functionalization with organosilanes. Of particular importance was that modification was conducted in water. Humates from coal and peat and 3-aminopropyl-triethoxysilane (APTES) were used as starting materials. Atomic force microscopy showed silanized HS produced self-assembled adsorption monolayers at the water–solid interface. These adlayers caused an increase in the surface hydrophobicity with contact angles equaling 56°. Application of silanized HS for treatment of different soil compartments including mineral soil separates and soil aggregates revealed an efficacy with respect to both re-assembly of soil aggregates and restoration of their water stability. Furthermore, field trials on the treatments of native sod-podzolic soil with silanized HS indicated improvements in soil structure as compared to non-treated soil or treatment with the non-functionalized humate. Results demonstrating the use of silanized HS as ecologically-safe, nature-inspired soil conditioners were promising.

1. Introduction

Soil aggregates provide one of the most striking examples of nanoarchitectures in nature. They play a crucial role in maintaining soil structure and in water retention capacity of soils (Bossuyt et al., 2005; Jastrow et al., 1996; Lal, 2004). Formation of soil aggregates is largely dependent on organic matter, generically known as humic substances (HS) (Angers and Giroux, 1996; Blanco-Canqui and Lal, 2004, Six et al., 1999, 2000; Bossuyt et al., 2005). According to hierarchical theory of aggregation (Tisdall and Oades, 1982, Oades and Waters, 1991), organic matter plays a key role in the formation of microaggregates (<0.25 mm) via attachment to clay and polyvalent cations to form organoclay complexes. Those, in turn, are joined with other microaggregates to form macroaggregates (Edwards and Bremner, 1967; Tisdall, 1996, Almendros and González-Vila, 1987). The bonds within microaggregates are stronger than the bonds between microaggregates (Edwards and Bremner, 1967). As a result, organic matter in microaggregates is much better protected against decomposition, bringing in substantially slower average turnover times compared with organic matter in macroaggregates (Balesdent et al., 2000; Besnard et al., 1996; Jastrow et al., 1996; Monreal et al., 1995; Skjemstad et al., 1996). This indicates crucial importance of microaggregate formation for long-term sequestration of organic carbon (OC) in soils (Bossuyt et al., 2005; Oades, 1984; Six et al., 1999, 2000).

Due to cultivation, cropping soils generally contain little organic matter and of much poorer quality as compared to native soils (Balesdent et al., 2000; Elliot, 1986). This is a consequence of the increased rate of organic matter destruction caused by cultivation practices which imply tillage and an intense use of mineral fertilizers (Bronick and Lal, 2005). It has been widely reported that HS in cultivated soils are characterized with the lesser content of aromatic carbon and increased contribution of oxidized aliphatic fragments (Besnard et al., 1996). In terms of hydrophobic–hydrophilic balance, the observed changes in the structure of humic molecular ensemble lead to an increase in its hydrophilic character. This, in turn, causes a decrease in the ability of HS in those soils to hydrophobize surfaces of clay particles. The latter phenomenon is of particular importance for self-assembly of

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* Corresponding author.
E-mail addresses: ab.volikov@gmail.com (A.B. Volikov), vkholod@mail.ru (V.A. Kholodov), knat@darvodgeo.ru (N.A. Kulikova), philolga@mail.ru (O.I. Philippova), ponomarenko@ispm.ru (S.A. Ponomarenko), lasareva@yandex.ru (E.V. Lasareva), parf@colloid.chem.msu.ru (A.M. Parfyonova), kirk.hatfield@essie.ufl.edu (K. Hatfield), iperm@org.chem.msu.ru (I.V. Perminova).

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microaggregates into water stable macroaggregates (WSMA) while hydrophilic organic coating cannot prevent macroaggregates from slaking (Zhuang et al., 2008). The beneficial role of hydrophobic amendments for restoring soil structure was demonstrated in the studies of Piccolo and Mbagwu (1999); Piccolo et al. (1997, 2004), and Goebel et al. (2007).

In this work we propose to use mineral-adhesive HS modified with organosilanes as soil amendments of new soil restoration technology directed both to intensifying microaggregates formation and to improving water stability of macroaggregates. These mineral-adhesive HS are obtained by incorporating organosilanes into humic molecular ensemble. As a result, silanized HS acquire capability to attach to clay particles and to produce hydrophobic adlayers onto their surfaces bringing about their hydrophobization, which is needed to sustain water-stability of soil aggregates and to improve soil structure. The general scheme of this process is shown in Fig. 1. To prove the proposed concept, the mineral-adhesive properties of the silanized HS were characterized using glass, clay, and degraded soil separates as soil mineral surrogates. The corresponding aggregation studies were conducted in the lab and in the field.

2. Materials and methods

2.1. Materials

Two types of humic materials with different origins were used in this study: from coal and from peat. Commercially available potassium humate (Sakhalin Humate) isolated from leonardite was used as a coal humic material and designated as CHS. Peat sodium humate (PHA) was obtained from low moor peat by single extraction with 1 M NaOH. Reagents of the analytical grade (NaOH, HCl, KH_2PO_4, and $Na_2HPO_4 \times 12H_2O$) were used for isolation and characterization of HS. The 3-aminopropyltriethoxysilane (APTES) was purchased from Penta Ltd. (Moscow). It was of technical-grade and used as is.

2.2. Functionalization and characterization of humic materials

The reaction stoichiometries were calculated as described in Perminova et al. (2012). A required aliquot of APTES in mL (e.g., 0.2, 0.5, 1,0) was added dropwise to the solution of 1 g humate in distilled water under continued stirring, and pH was adjusted to 4 using conc. HCl. Then, the reaction mixture was rotor-evaporated to dryness, and the residue was further dried in a vacuum oven at 120 °C for 6 h. The reaction scheme and modification diagram are shown in Fig. 2A and B, respectively. The resulting products were designated as CHS-APTES-X or PHS-APTES-X, where X is equal to 20, 50, or 100, depending on the modification degree. The modified humic materials were analyzed for the content of elements (C, H, N) using a Varo EL Elementar. The Si content was determined using spectrophotometric method as described elsewhere (Carlson and Banks, 1952). Ash content was determined by manual combustion. Oxygen content was calculated as a difference. Carboxylic acidity was determined using Ca-acetate technique (Swift, 1996).

2.3. Sorption of the silanized HS onto glass and clay minerals

Borosilicate glass slides from Borofloat (Schott Nexterion) were used, these are specifically manufactured to suit DNA arrays with minimum surface roughness. The modification protocol is described by Karpiouk et al. (2012). The silanized humic materials were applied on the activated slide surfaces as solutions in phosphate buffer (0.03 M, pH 6) at concentrations of 1 g L^{-1}. The morphology of the self-assembled humic adlayers was investigated by atomic force microscopy (AFM) at room temperature with Integra (NT-MDT) controller. The imaging was done in Tapping Mode using standard silicon cantilevers. The hydrophobicity was determined by measuring the contact angle of a water drop on the glass surface using photomicrographs.

Sorption experiments were conducted for two clay minerals - kaolinite and montmorillonite. Stock solutions of HS were prepared with concentrations of 10 g L^{-1} in the presence of 0.001 M $CaCl_2$. An aliquot (5 mL) of this stock solution was added with 8 mL of clay suspension containing 0.1 g of clay on the solid weight basis. The equilibrium time was 48 h. HS concentration was monitored by measuring optical density at 254 nm using UV–Vis spectrometer (Cary 50, Varian Inc., U.S.A.).

2.4. Laboratory testing of soil separates treated with silanized HS

The sample of loamy arable Retisol (World reference base for soil resources (WRB), 2014) was collected near Zelenograd, a town in the Moscow Region of Russia. It has a content of organic C of 13.8 g kg, and pH 6.8. The soil was dry sieved, and microaggregates with sizes <0.25 mm, and macroaggregates with sizes from 3 to 5 mm, were collected and treated similar to the approach described by Kholodov (2013). In brief, a weight of 20 g of microaggregates was placed into a Petri dish and added with 20 mL of test HS solutions (2.5 and 5 g L^{-1}). The obtained suspensions were air-dried and shaken for 1.5 h in a centrifuge tube. The self-assembled aggregates were separated by dry sieving into the macro (>0.25 mm) – and micro (<0.25 mm) – aggregates, and the content of WSMA was determined by wet-sieving. Percentage of WSMA was calculated from the mass of initial soil.

The macroaggregates were treated with the silanized HS and their water stability was assessed using the Andrianov test (Milanovskiy et al., 2013, Shein et al., 2007, 2009). The fifty macroaggregates were evenly distributed over the filter paper in the Petri dish, capillary-saturated with water, and air-dried. Then, water was carefully added to the half-height of the Petri dish, kept for 10 min, and the amount of slaked aggregates was counted. The ratio of WSMA was calculated by the following formula:

$$K = \frac{\sum_{t=1}^{9} (c-a) * \left(\frac{t-1}{10} + 0.05\right) + b}{c} \quad (2)$$

where t is the number of minutes, a is the number of slaked aggregates per minute, b is the number of water-stable macroaggregates, and c is the total number of aggregates.

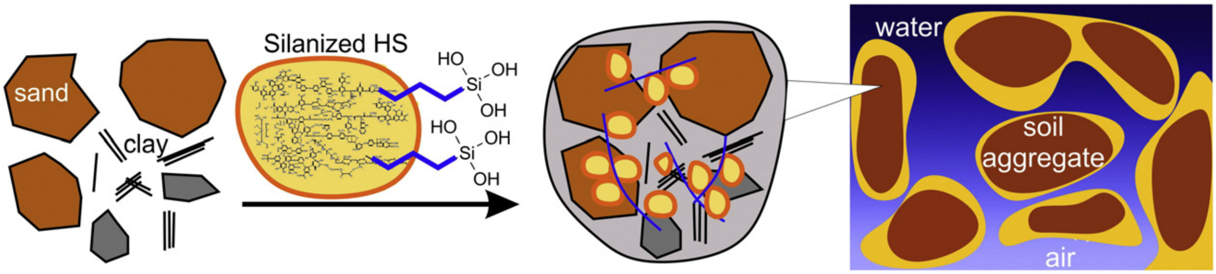

Fig. 1. Schematic representation of the silanized humic materials acting as binding agents for soil particles facilitating their assembly into water proof soil aggregates.

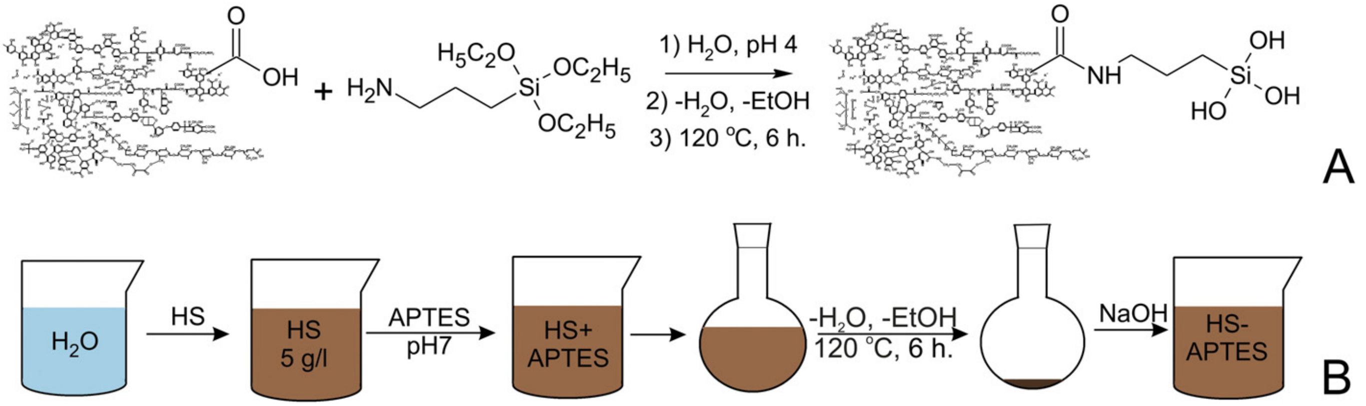

Fig. 2. The reaction scheme of modification of humic materials with the use of 3-aminopropyltriethoxysilane using water as a solvent (A) and the corresponding modification diagram (B).

2.5. Field tests

Field site was located in Yaroslavl' Region, Russia (56.856927, 38.295715) on fallow land of Retisol soil (World reference base for soil resources (WRB), 2014). The climate is humid with average annual rainfall of 590–600 mm. The soil (0–5 cm) samples were silty loam with pH 6.9, the content of organic C — 29.9 g kg^{-1}, K_2O — 110 mg kg^{-1}, and P_2O_5 — 490 mg kg^{-1}. The plots were 1 m^2 each. CHS and its APTES-derivative (CHS-APTES-50) were introduced into soil as watering solutions (10 L m^{-2}) with concentrations of 2.5 g L^{-1}. The same amount of tap water (10 L m^{-2}) was applied to the blank plots. The watered plots were sowed with wheat (500 seeds m^{-2}). The trial was performed in triplicates. The soil samples of 1000 g were collected in triplicates from each plot at 0–5 cm before and after the beginning of the experiments (three and twelve months later) for determination of the content of WSMA according to (Korchagin et al., 2011). An air-dried soil sample was dry-sieved into fractions with sizes (in mm) >10, 1–10, 0.25–1, and <0.25. The obtained fractions were wet-sieved, and the percentage of WSMA in the fractions with sizes >0.25 mm was calculated from the mass of initial soil.

2.6. Statistical analysis

The contents of WSMA fractions were analyzed using a two-way ANOVA analysis with "treatment" and "sampling time" as two fixed factors. The calculated F-ratio statistics (F), a critical value from a probability table (F_{crit}) at calculated probability P were derived from the ANOVA. The comparison of F and $Fcrit$ was used to assess statistical significance of the factors. A least significant difference test (LSD) was used for comparison between paired means at $P < 0.05$.

3. Results

3.1. Surface modifying properties of silanized HS

Functionalization of HS by organosilanes is aimed at overcoming poor affinity of humates for sorption on hydroxyl-carrying surfaces, such as silica gel, clay, sand, glass, and other materials. Previously, we have shown that this can be efficiently achieved by the incorporation of alkoxy groups into humic backbone using treatment of protonated humic acid with aminoorganosilane in the organic solvent dimethylformamide (Karpiouk et al., 2012): sorption affinity of the resulting alkoxysilyl-humic derivatives achieved 220 mg g^{-1} of silica gel. However, the use of organic solvent posed a major problem for environmental applications of these derivatives.

Because of this, we modified the method and conducted the modification of the HS with aminoorganosilane using water as solvent. We have obtained six silanized humic materials (listed in Table 1) and concentrated on estimating the surface activity of these materials. To enable studies on morphology and hydrophobicity, they were immobilized on the glass slides. The general immobilization scheme and the results of this study are visualized in Fig. 3.

The morphologies observed in Fig. 3B can be described as a monomolecular adlayer segregated into separates with diameters from 10 to 100 nm with heights from 5 to 10 nm. The presence of single separates up to 20 nm can be explained by settlement of silica sol particles which can form due to partial hydrolysis of humic silanol derivatives in aqueous solutions. The discrete character of the adlayer might reflect scarceness and uneven distribution of binding sites on the glass surface which are formed during its activation.

Also contact angle measurements were taken before and after the modification of glass with the silanized HS. Typical microphotographs are shown in Fig. 3C. and the recorded values summarized in Table 1 together with the elemental and functional group compositions of the derivatives. The hydrophobicity of glass grew significantly with the degree of derivative modification up to 50%. Greater degrees of modification up to 100% were not accompanied by corresponding increases in glass hydrophobicity. This could be explained by the excessive amount of silanol groups which were not used in covalent bonding to the glass surface for the highly modified humics. This phenomenon was observed both for coal and peat humic derivatives. At the same time, peat humic derivatives produced less hydrophobic coatings as compared to those of coal. This finding is consistent with the higher aromaticity of CHS as compared to PHS as indicated in corresponding H/C values given in Table 1. Maximum values of hydrophobicity were reached with CHS-50 and PHS-50 derivatives, which allowed us to consider 50% as the optimum degree of modification for the further studies.

The sorption isotherms of the silanized HS onto kaolinite and montmorillonite are shown in Fig. 4 and the corresponding sorption parameters are summarized in Table 2. The data obtained clearly indicate substantial increases in the sorption capacity of the silanized HS with respect to both types of clay minerals, as compared to the parent humate. A modification degree of 50% (shown for CHS-APTES-50) induced a

Table 1
Structural and molecular weight characteristics of the humic materials.

Name	C, %	Si %	H/C	C/N	COOH, mmol g^{-1}	Contact angle (deg)
CHS	31.7	6.3	1.08	0.04	2.7 ± 0.1	40 ± 4
CHS-APTES-20	32.4	6.4	1.20	0.05	2.4 ± 0.4	48 ± 5
CHS-APTES-50	31.6	7.5	1.34	0.08	2.0 ± 0.3	56 ± 6
CHS-APTES-100	31	8.8	1.48	0.11	1.8 ± 0.4	52 ± 4
PHS	40.9	0.6	1.2	0.08	2.9 ± 0.2	40 ± 4
PHS-APTES-20	40.1	2.1	1.30	0.09	2.2 ± 0.4	42 ± 4
PHS-APTES-50	38.8	4.4	1.33	0.11	2.4 ± 0.4	52 ± 3
PHS-APTES-100	31.4	5.5	1.46	0.14	1.7 ± 0.4	48 ± 4

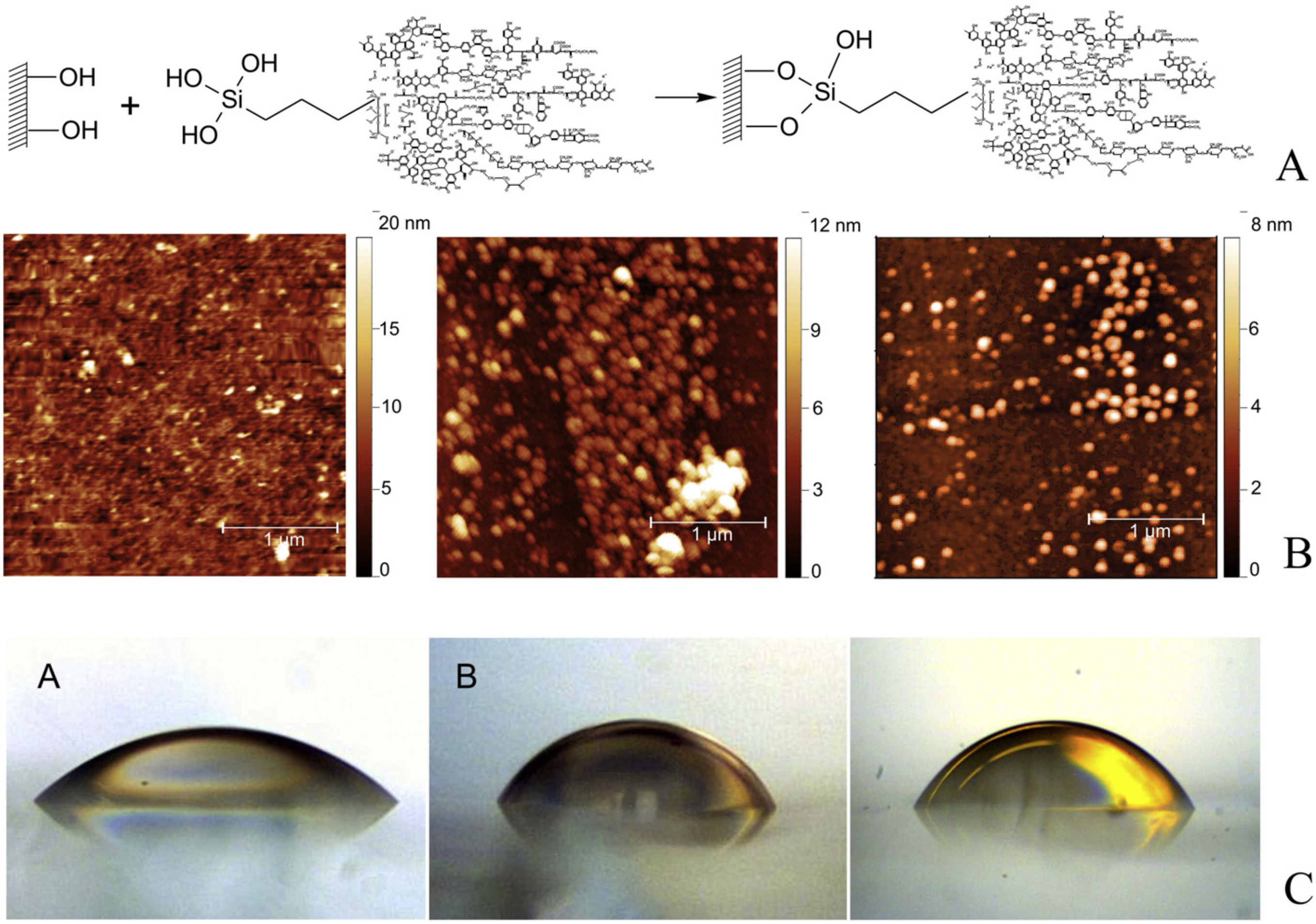

Fig. 3. Modification of the glass surface with the humic adlayers: A) general scheme of immobilization of the silanized humic materials onto the hydroxyl-carrying surfaces; B) AFM images of the glass surface modified with the silanized humic materials: the original glass (left) CHS-APTES-50 (middle) and PHS-APTES-50 (right); C) microphotographs of a drop of water on the glass surface modified with the silanized humic materials: the original glass (left), the glass modified by CHS –APTES-50 (middle); the glass modified with PHS-APTES-50 (right).

twofold increase in maximum sorption both for kaolinite and montmorillonite. Data for kaolinite (Fig. 4A) show that a further increase in modification up to 100% (CHS-APTES-100) was accompanied by a linear growth of sorption starting with equilibrium concentrations exceeding 0.4 g L^{-1}. This might be indicative of the beginning of multilayer sorption caused by aggregation processes in the concentrated solutions of the silanized derivatives with a high degree of modification. To avoid an impact of the poorly controlled aggregation processes on experiments, we used silanized derivatives with 50% modification for further laboratory and field testings of soil separates.

3.2. Aggregating properties of soil separates treated with the silanized-HS

Based on the obtained results, we believed that by applying silanized HS to soil separates we can induce formation of macroaggregates with higher content of organic matter and of increased hydrophobicity. To

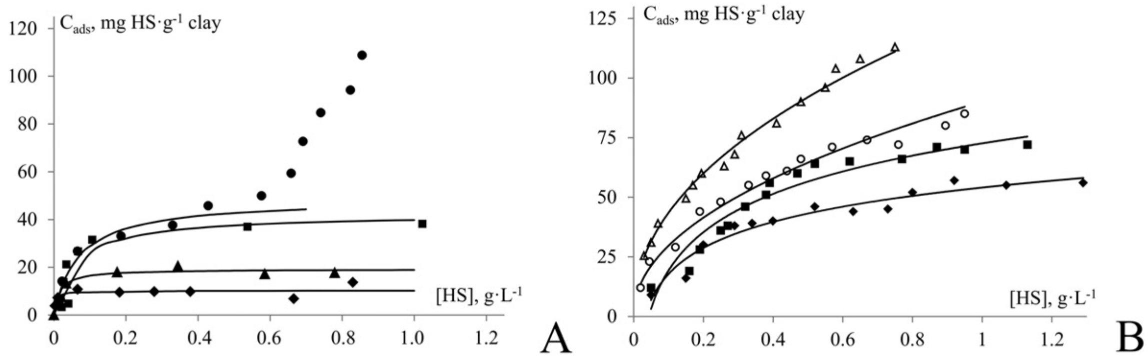

Fig. 4. Sorption isotherms of the silanized HS onto kaolinite (A) and montmorillonite (B). Designation of the humic samples sorbed onto kaolinite is as follows: solid diamonds (♦) — parental humate from coal (CHS), solid triangles (▲) — CHS-APTES-20; solid squares (■) — CHS-APTES-50; solid circles (●) — CHS-APTES-100. Sorption onto montmorillonite was conducted onto raw and activated clay designated with hallow and raw marks, respectively: (♦) and (○) — CHS; (■) and (◇) — CHC-APTES-50.

Table 2
Sorption parameters of the silanized humic materials onto kaolinite and montmorillonite.

Samples	Q_{max}, mg HS g^{-1} clay	K_{S}, L g^{-1}	R^2
Kaolinite			
CHS	10 ± 1	5 ± 0.2	0.942
CHS-APTES-20	19 ± 1	17 ± 1	0.825
CHS-APTES-50	42 ± 2	65 ± 3	0.812
CHS–APTES-100	49 ± 2*	69 ± 2*	0.959
Raw montmorillonite			
CHS	81 ± 2	2.9 ± 0.2	0.985
CHS-APTES-50	118 ± 3	2.0 ± 0.2	0.980
Activated montmorillonite			
CHS	107 ± 2	3.7 ± 0.2	0.977
CHS-APTES-50	153 ± 3	3.4 ± 0.2	0.955

* Sorption characteristics were calculated using data until equilibrium concentration of 0.4 g L^{-1}.

prove this hypothesis, we have treated soil particles with sizes <0.25 mm with solutions of the silanized HS (CHS-APTES-50) and initial humate (CHS). The best results were obtained for the silanized HS solution with a concentration of 5 g L^{-1} where nearly 20% of the initial soil separates were capable of self-assembly into WSMA (Fig. 5). At the same time, application of water and of parent humate did not induce substantial aggregation. Hence, results indicate that the silanized HS are capable of enhancing aggregation processes in soils, in particular, bringing about formation of WSMA.

In order to test the effect of the treatment with silanized HS in the water stability of macroaggregates already present in the soil, we used the isolated soil aggregates (3 to 5 mm in size) from the same sample of Retisol. The isolated aggregates were also treated with distilled water and with the solutions of CHS-APTES-50 and initial humate. The kinetics of aggregate slaking are presented in Fig. 6 which shows photos of the experiments before and after addition of water (Fig. 6A) and the corresponding kinetic curves (Fig. 6B). Results show that substantially higher water stability was observed for the aggregates treated with the silanized HS as compared to initial humate or distilled water: the corresponding water stability coefficients accounted for 0.51, 0.22, and 0.27.

3.3. Field applications of the silanized humic derivatives

To prove if the above beneficial effects of silanized HS will be seen under field conditions, we conducted field trials using treatments with CHS-APTES-50. Our field trials demonstrated that the content of WSMA in the soil studied was influenced both by treatments with the silanized HS ($F = 10.72$, $P = 3 \times 10^{-4}$, $Fcrit = 3.32$) and by the sampling time ($F = 64.56$, $P = 6 \times 10^{-9}$, $Fcrit = 4.17$). No interaction between those factors was observed ($F = 0.79$, $P = 0.46$, $F_{crit} = 3.32$). The obtained results (Fig. 7) show that three months after the beginning of the trial, an increase in the content of WSMA was observed up to 121–137% as compared to before treatments reaching its maximum values in the soil treated with CHS-APTES-50. This confirms the capacity of the tested silanized HS to facilitate formation of the water-stable aggregates in the field.

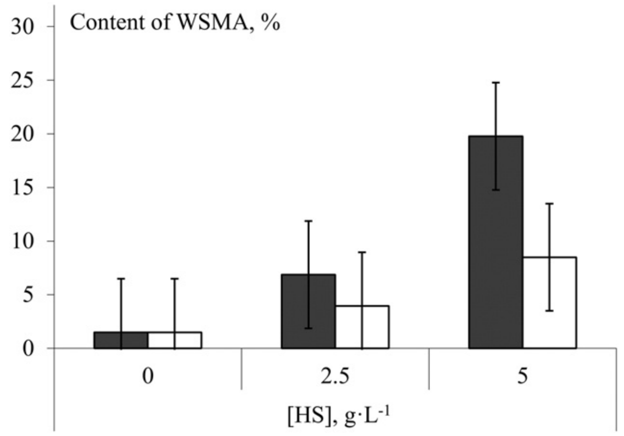

Fig. 5. Self-assembly of soil particles with sizes <0.25 mm into water-stable macroaggregates (WSMA) after treatment with the different concentrations of the silanized HS (CHS-APTES-50), and the initial potassium humate (CHS) expressed as percentage of initial soil shown in dark and white color, respectively.

Determination of WSMA in the same experiments a year later showed a decrease in the content for all treatments. The most drastic decrease was observed with blank soil (from 121 down to 85), while for soil treated with the parent humate (CHS) and, in particular, for its silanized derivative (CHS-APTES-50) this effect was less pronounced (from 137 down to 112 in the latter case). A loss of water-stable aggregates over time might suggest the need for repeated treatments. On the other hand, the content of WSMA was still significantly higher as compared to the blank indicating good prospects for the use of silanized HS as soil amendments.

4. Discussion

Humic materials which were modified with aminoorganosilane in aqueous phase to acquire mineral adhesive properties were used in this study as soil amendments. It was shown that the undertaken modification lead to substantial enhancement of surface activity of the parental HS both in case of coal and peat HS. So, the silanized HS were capable of self-assembly in adlayers onto glass surface whose AFM-images were very similar to those observed for the natural humic colloids immobilized onto mineral surrogates (e.g., mica) (Liu et al., 2000). The obtained humic adlayers were composed of unevenly distributed separates with flat particle morphologies with the larger separates in case of peat HS (10–20 nm) and smaller separates (8–13 nm) — in case of coal (Fig. 3B). Similar sizes for the immobilized HS were estimated by Barbot et al. (2007). The structural differences in the parental HS determined also hydrophobicity of the HS-modified glass surface: it was higher in case of the aromatics enriched coal HS as compared to the carbohydrates enriched peat HS. The observed trend as well as the determined values of the contact angles are consistent with the data reported by (Yuan and Zydney, 2000) and (Plakas and Karabelas, 2011) who measured contact angles of the ultrafiltration membranes before and after filtration of fulvic and humic acids of different origin. According to the reported data (Yuan and Zydney, 2000), the value of the contact angle of clean membrane accounted for 44 ± 4° and increased up to 74 ± 4° after filtration of Aldrich humic acid, and up to 53 ± 2° after filtration of the Suwanne River fulvic acid. The authors explain the observed effect by higher hydrophobicity of the coal humic acid as compared to the riverine fulvic acid. Similar data were obtained by (Plakas and Karabelas, 2011) who filtered humic and fulvic acids through hydrophobic and hydrophilic membranes: they observed hydrophobization of the hydrophilic membrane (an increase in the contact angle from 28° to 48°) after its fouling with the humic acid, and, vice versa, hydrophilization of the hydrophobic membrane (a decrease in the contact angle from 62–65° down to 52–57°). It should be noted that the reported values of the contact angles of the membrane surfaces covered with the humic adlayers were very close to those obtained in this study for glass covered with the humic adlayers: for less hydrophobic peat HS it varied from 42 to 52°, and for more hydrophobic coal HS — from 48 to 56°. Hence, these results might be very instructive for the proper choice of the raw humic material for the soil amendment purposes.

The silanized HS displayed substantially higher sorption affinity for the clay minerals: the values of sorption capacity accounted for 50 and 120 mg g^{-1} for kaolinite and montmorillonite, respectively, whereas the corresponding values for the non- modified HS accounted for 10 and 80 mg g^{-1}. The similar values for the non-modified HS were reported by (Balcke et al., 2002, Feng et al., 2005; Salman et al., 2007), The

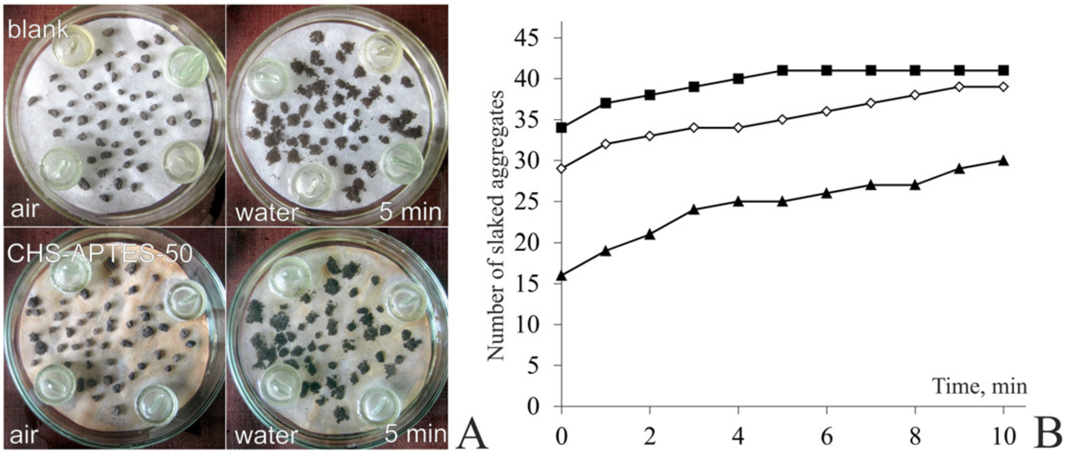

Fig. 6. The slaking kinetics of soil aggregates (sizes from 3 to 5 mm) treated with water, the coal humate (CHS), and the silanized HS (CHS-APTES-50). A) Photographs of non-treated (upper row) and CHS-APTES-50 - treated (bottom) aggregates before and after addition of water; B) Kinetic curves of aggregate slaking upon water addition. Solid triangles (▲) represent aggregates treated with CHS-APTES-50, solid squares (■) — treated with CHS, and void circles (○) — treated with water.

specific advantage of the proposed approach is that it allowed us to attain efficient immobilization of high amounts of HS (up to 150 mg g^{-1}) onto clay minerals without preliminary modification of the mineral phase: the comparable values were reported by other authors only for the aminated substrates (e.g., aminated silica gel (Koopal et al., 1998), amine-modified-polyacrylamide-bentonite (Anirudhan et al., 2008)). Of particular importance is that the synthesis of the corresponding humic derivatives did not imply the use of organic solvent: modification of HS occurred in water, which makes applicable their use in soils.

Application of the silanized HS as soil amendments has demonstrated an increase in the number of WSMA during the vegetation period followed by its decrease after a year of soil treatment. The most drastic decrease was observed with blank soil, while for soil treated with the parental HS or its silanized derivative this effect was less pronounced (Fig. 7). This finding is in agreement with the hierarchical theory of aggregate formation proposed by Tisdall and Oades (1982), who classified organic amendments used for improving soil structure into three groups: transient, temporary, and persistent. This classification is based on longevity of the amendment and on the persistence of its effect on aggregate stability. Transient and temporary binding agents are of predominantly aliphatic character composed of exudates of microbial biomass, roots, and fungal hyphae, whereas persistent binding agents are of predominantly aromatic character consisted of decomposed lignin and humic materials. The transient and temporary binding agents are mainly associated with large (>0.25 mm) transiently stable macroaggregates, whereas persistent binding agents are important component of microaggregates (0.02–0.25 mm). Macroaggregates stabilized by transient and temporary agents are drastically affected by soil biota activity and persist for few months (up to a year). On the contrary, microaggregate complexes are considerably more stable.

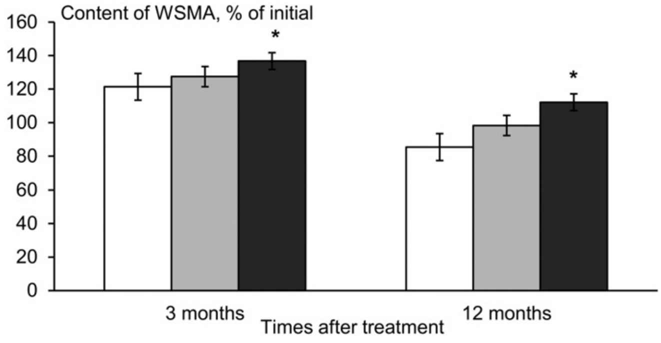

Fig. 7. Content of water-stable macroaggregates (WSMA) in Retisol measured 3 and 12 months after application of water, the coal humate (CHS), and the silanized HS (CHS-APTES-50) shown in white, grey, and black color, respectively. An asterisk * indicates statistically significant difference from blank value.

The results on field applications of the silanized HS are consistent with this theory. It looks like the observed variation in WSMA content in the soils treated with water was related mainly to alteration of microbial activity and root development. On the other hand, when the same soil was amended with the parental or the silanized humic materials, the enhanced formation of WSMA could be considered as inducing persistent effects. It should be emphasized that after one year after the soil was amended with the parental HS, the WSMA >0.25 mm content decreased to its initial amount (98%). The latter finding corroborates well the numerous data that HS act as stronger stabilizers of microaggregates as compared to macroaggregates. So, the reported studies (Piccolo et al., 1997; Yamaguchi et al., 2004) demonstrated significant correlation of microaggregate stability with the HS content in soil, which is supportive of the idea that HS are the predominant binding agents in this aggregate range. In case of the silanized HS, however, the number of WSMA >0.25 mm in soil exceeded the initial value after one year of introduction. This could be explained by the moderate hydrophobization of the hydrophilic mineral surfaces modified with the silanized humic materials (Table 1). Orientation of the hydrophobic components of humic molecules toward the outside of the aggregate was hypothesized to reduce water infiltration and, thereby, to increase the soil macroaggregate stability (Piccolo et al., 1997; Plaza et al., 2015). As a result, the soil resistance to the disaggregating effect of wetting-drying cycles has increased (Piccolo et al., 1997). The recent study by Plaza et al. (2015) showed that HS increased surface free energy component related to hydrophobicity of soil material from 39.6 to 48.3 mJ m^{-2}. That effect was attributed to the higher aggregation state in soil samples with added HS. Hence, hydrophobization of mineral soil particles due to adsorption of organic materials seems to be a plausible mechanism for formation of WSMA. The above considerations, as well as the results obtained in this study, enable us to suggest that WSMA can be considered as a special kind of Pickering emulsion, in which droplets of water are stabilized against air with organomineral solid particles. The latter should be hydrophobic to sustain water stability of aggregates. The formation of water in air emulsion stabilized by hydrophobized particles of silica gels (called “dry water”) has been reported by Binks and Murakami (2006) who observed direct relationship between emulsion stability and hydrophobicity of the stabilizer. Similar forces might contribute to in situ formation of WSMA which is enhanced in the hydrophobic soil domains (Vogelmann et al., 2013).

In view of turning agricultural soil into a sink for organic carbon (OC), another benefit resulting from hydrophobization of soil with the silanized humic materials should be considered. At present, there is a general consensus on the involvement of multiple hydrophobic interactions among HS and fresh organic compounds as the main reason for refractory character of HS and their long-term accumulation in soils. It is thus conceivable that humic material of appropriate composition may reduce OC mineralization in soil by increasing its sequestration into hydrophobic domains. A process of hydrophobic protection should thus prevent rapid microbial decomposition of the labile organic matter entering the soil with litter or plant residues (Spaccini et al., 2002). In support of this view, Piccolo et al. (2004) reported results of one year experiment confirming that labile organic matter (polysaccharides) in soils can be protected from biodegradation by repartition into the hydrophobic domains of the stable humified organic matter. So, the further studies of the silanized humic materials as prospective OC sequestration amendments are needed.

5. Conclusions

We have demonstrated in the lab and in the field that silanized HS enhanced the formation of water stable soil macroaggregates (WSMA). As a soil restoration technology it showed promise. The technology does not include the use of any harmful reagents which could compromise their ecological safety. To the best of our knowledge, this is the first direct demonstration of how the solubility limitations of alkaline metal humates might be addressed with an environmentally sound chemical modification and with particular consideration given to the moderate hydrophobization of the hydrophilic surfaces with silanized HS. The latter phenomenon enabled us to suggest a new vision whereby WSMA represent a special kind of Pickering emulsion in which droplets of water are stabilized against air with organomineral solid particles. While air serves as dispersion medium in soil, the hydrophobic solid stabilizers sustain stability of this structure. At this stage of the research, the proposed concept is more an interesting analogy than a robust scientific hypothesis, but it might shed new light on mechanisms of waterproof aggregate formation in soils. It might also explain an efficacy of hydrophobic amendments for restoring the water retaining capacity of soils. In this context the silanized humic derivatives might prove useful as molecular probes in such studies.

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