

## Chapter 10

# Contact Angle Hysteresis in the Clay-Water-Air System of Soils



Oxana A. Sofinskaya, Akhmet A. Galeev and Eduard A. Korolev

**Abstract** Microorganisms emit substances changing the surface tension of soil solution and the surface energy of solid soil particles. Clays and soils have high heterogeneity of the surface energy distribution among particles. The change in the surface energy of soil particles is caused not only by alteration of their chemical properties but also an increase/decrease in their spatial heterogeneity, which determines contact angle hysteresis. Available techniques of measurement the contact angle and the contact angle hysteresis require further improvement and adaptation to specific clay types. The purpose of this research is to study the change in wettability of clays due to the influence of mesophilic soil microorganisms' activity when adding model contaminants: water-in-oil emulsion, glycerol and oleic acid. During the experiments, the objectives of this study were to specify peculiarities of wetting contact angle hysteresis of clays with substrates of different mineral composition and microbial activity. Hydrophilicity/hydrophobicity of the stimulator for microbial activity does not have a clear effect on clay properties. The surface heterogeneity mostly increases with time, perhaps, due to biofilm exudates whatever was a type of microbial stimulator. Chemical and geometric heterogeneities played comparable roles in the surface hydrophilic-hydrophobic balance. Results obtained prove that microbial communities and/or the Fe chemical state alteration (pyrite, hematite or goethite) were responsible for both hydrophilization and hydrophobization of the surface. The equation for the drop spreading rate was presented and verified by well comparison of experimental results with simulations.

**Keywords** Biomat · Biofilms · Hydrophobicity · Hydrophilicity · Clay minerals · Surface tension · Contact angle · Hysteresis of wettability · Water spreading · Water repellency

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## 10.1 Introduction

Microbial communities as an indispensable part of soils play an important role in regulating hydrophysical properties. Microbial communities control such processes as the formation of water-stable aggregates, the decrease in the specific surface area of soil and soil constituents, high mechanical pressure zones created by growing fungal hyphae (up to 10–100 MPa), which destroys the solid rock, the exudation of acids, which affect the pH of porous solution, the dissolution and precipitation of minerals, the formation and transformation of clay minerals (Rockhold et al. 2002; Zhu et al. 2011; Shein et al. 2016; Cuadros 2017). Microorganisms emit substances changing the surface tension of porous solution (particularly soil solution) and the surface energy of solid soil particles (Bachmann et al. 2003; Shang et al. 2008; Tyugai and Milanovskiy 2015; Shein et al. 2016). The change in the surface energy of soil particles is caused not only by alteration of their chemical properties but also an increase/decrease in their spatial heterogeneity, which determines contact angle hysteresis (CAH). CAH can be measured by means of different techniques (Kirichenko and Gatapova 2016). Accumulated data allows one to simulate physical mechanisms of wetting behavior of different soil minerals and aggregates (Zhang et al. 2016; Fer et al. 2016). However, existing CA and CAH measurement techniques require further improvement and adaptation to specific clay types.

Wettability can be estimated in a laboratory by measuring CA of water droplets on different solid surfaces. Contact angle depends on the polarity of interacting molecules and their fragments. The interaction of complex multicomponent molecules with water in the soil can exhibit both hydrophilic and hydrophobic properties simultaneously. Polar parts of such molecules ( $-\text{OH}$ ,  $=\text{CO}$ ,  $-\text{S}$ ,  $=\text{O}$ ,  $-\text{NH}_2$ ,  $-\text{F}$ ,  $=\text{N}-\text{OH}$ ,  $-\text{NO}_2$ ,  $-\text{N}=\text{O}$ ,  $-\text{C}=\text{N}$ ,  $-\text{N}=\text{N}-\dots$  and non-polar  $-\text{C}_6\text{H}_5$ ,  $-\text{CH}_3$ ,  $-\text{CH}=\text{CH}_2$ ) are subjected to hydration while the non-polar ones can only influence the wetting liquid (Krestov and Berezin 1986). The hydrophilic and hydrophobic interaction in soil contributes some unpredictability to the surface properties depending on the previous wetting history, which is usually unknown. The presence of aqueous or non-aqueous film on clay surfaces influences the orientation of adsorbed molecules and, thus, the exhibition of hydrophilic or hydrophobic properties even after eliminating this film. The more clearly the effect of hydrophilic-hydrophobic interactions manifests itself, the longer the film/clay contact history is. In the wild, this prehistory will be characterized by zonality associated with the development of biofilms.

Clays and soils have high porosity and surface roughness, i.e. high heterogeneity of the surface energy distribution among particles. Clays are strongly hydrophilic in nature with zero contact angle representing complete wetting. However, there are a number of factors in practice that leads to CAH, which could be determined in two ways: (a) as difference between advancing and receding CA; (b) as difference between static and initial contact angles. Thus, the following kinds of CA are observed when a liquid droplet spreads over a solid soil surface (Summ and Gorjunov 1976; Bonn et al. 2009):

- equilibrium CA is related to the ideal (smooth, homogeneous, rigid and insoluble) solid; hereby, it is considered when rough surfaces are wetting;
- static CA is measured without changing the contact area between liquid and solid; it is often more meaningful for assessing quasi-static processes;
- dynamic CA depends on the solid/liquid contact time; the local angle the interface makes with the substrate depends strongly on scale, i.e. on the distance from the contact line; occurs in the course of wetting (advancing angle) or de-wetting (receding angle) of a solid;
- two senses of apparent CA (macroscopic angle):

$\cos \theta_w = r \cos \theta$ —Wenzel-Derjaguin CA (Wenzel 1936; Derjaguin 1946),

$\cos \theta_{CB} = \sum \lambda_i \cos \theta_{Yi}$ —Cassie-Baxter CA (Cassie 1948),

where  $\theta$  is Young's contact angle as defined for the ideal surface,  $\theta_{Yi}$  are Young's angle of the material  $i$ , including air for rough surfaces,  $r$  is the roughness parameters,  $\lambda_i$  is the area fraction of the material  $i$  on the surface.

Properly speaking, in case of clayey soils, we deal with apparently dynamic CA on the heterogeneous wetting surface. In practice, the estimation of CA is related to the measurement of drop spreading and absorption (and sometimes evaporation) rates. During the sessile drop spreading time, a film with a thickness ranging from several dozen angstroms to several micrometers appears, and the drop mass starts spreading (Summ and Gorjunov 1976). Due to the porous structure of clays, liquid absorption is inevitable, and the drop spreads faster. Water drop evaporates much slower in normal conditions and, therefore, it can be neglected in the CA measurement.

A common way of studying soil wettability is to prepare powder specimens, which are sometimes pressed in a particular way. Nowadays this is the best way, though the problems of preferred orientation of clay particles and pores, their inclination to swell and crack during drying have not been solved yet (Arkhipov et al. 2012). When working with clays, it should be kept in mind that the scale of surface roughness is considered too small compared to a drop size. Consequently, the drop volume used for the CA measurement must be large enough on the surface roughness scale, but the pressure on the support must small enough for capillary forces to prevail over gravity.

Despite the fact that microbial communities play a key role in transforming soils, they are so strongly limited by their environment that more than 95% of them are in the latent state. In an active state, microorganisms of different taxonomic groups form biofilms consisting of extracellular polymeric substances create a biofilm on soil particles, which facilitates the extraction of necessary ions from minerals, provides the distribution of microbes on the soil surface and increases the adhesion of biomat (Gorbushina 2007—fata Morgana for co-author AAG). Such a biofilm controls the wettability of particular soil localities. Herewith, a biofilm-covered surface area plays a greater role than biofilm thickness. Coating the hydrophilic quartz particles in a thin film of biopolymer prevents water from spreading over the surface, and water tends to be pulled into a spherical drop (Cuadros 2017). When making a rough estimate for biopolysaccharide consisting of glucose residues, 1–20 mg per gram of polymer

will be enough to complete coating the quartz grains in powder, with a specific surface area ranged from 3 to 60 m<sup>2</sup>/g. It is known that when soil microbial activity develops over a long time, the surface of clay particles and micropores is completely covered with microbial extracellular products. However, one can expect that the increase in soil hydrophobicity caused by microorganisms is observed only when the soil initially exhibited high hydrophilic properties. In other cases, the result of the change in the soil surface energy depends on local interactions between biofilm and the hydrophobic substrate, which in the long run will likely to be consumed. It should be noted that this scenario of the change of the hydrophilic-hydrophobic properties of soils hasn't been explored yet. Contamination of soil with hydrocarbons can be an example. It is biodegradation that includes several stages. Each of these stages has a product different from its precursor in hydrophilic/hydrophobic properties, namely alcohol—an aldehyde/ketone—a fatty acid—a shorter carbon chain hydrocarbon (Salanitro 2001). The mathematical model of this process is in good agreement with the experiment (Lubysheva et al. 2018).

The **purpose** of this research is to study the change in wettability of clays due to the influence of mesophilic soil microorganisms' activity when adding model contaminants: water-in-oil emulsion, glycerol and oleic acid. During the experiments, the objectives of this study were to specify peculiarities of wetting contact angle hysteresis of clays with substrates of different mineral composition and microbial activity.

### 10.1.1 *Objects and Methods*

To model the microbial modification of water-soil systems we used the clayey samples with different mineral composition and surface energies depending on their natural compaction and transformation history (Fig. 10.1):

- (A) Colloidal silica (CS);
- (B) Luvic Chernozem, Loamic, Pachic, layer 0–20 cm (LC);
- (C) Chlorite-muscovite marl (CM);
- (D) Chlorite-muscovite marl with pyrite (CMP);
- (E) Muscovite-kaolinite calcareous clay with pyrite (MKCP);
- (F) Phyllite (Ph).

CS and LC possess the maximum and Ph—the minimum surface energy among the samples.

**Methods.** The mineral composition of samples was characterized by powder X-ray diffraction (Bruker D2 Phaser). The grain size distribution was measured by using the sieve, the sedimentation and the laser diffraction (Fritch Analysette 22) methods. Porosity coefficient was measured using water picnometer. Moisture content was defined gravimetrically. Organic matter content was measured using dry combustion method after pretreatment with acid to remove carbonates.







Clay sample		colloidal silica	chlorite-muscovite marl with pyrite	chlorite-muscovite marl	muscovite-kaolinite calcareous clay with pyrite	phyllite	Luvic Chernozem, Loamic, Pachic
Sample designation	Microbial community with glycerin stimulation	CS+G	CMP+G	CM+G	MKCP+G	Ph+G	-
	Microbial community with crude oil stimulation	CS+Oil	CMP+Oil	CM+Oil	MKCP+Oil	Ph+Oil	LC
	Microbial community with oleic acid stimulation	-	-	-	-	-	LC+OA
Total carbon content, % in dry weight		-	4,28 (>95% inorganic)	5,91 (>95% inorganic)	3,08 (>95% inorganic)	4,66 (>95% inorganic)	3,55 (>95% organic)
Clay absorbency on the example of dye methylene blue, absorbed for one hour							
Porosity after watering, % in volume		33	7	3	12	12	55
Particle size distribution, % in dry weight	>50 mcm	1	-	-	-	59,9	-
	10-50 mcm	66	58,3	71,3	26,3	24,0	35,5
	1-10 mcm	33	34,7	28,0	50,0	14,8	51,4
	<1 mcm	-	7	0,8	23,7	1,4	13,1
Full water capacity, % in dry weight		583	59	44	49	55	60
Maximum hygroscopicity, % in dry weight		27	4	2	5	2	6

Fig. 10.1 Clay samples characteristics and experimental options

**Experiment with microbial communities.** Air-dry samples were crushed in an agate pounder to a powder consistency. The samples were placed into Petri dishes distributing them at the bottom about 2 mm thick and wetted with distilled water and kept the total moisture capacity at the level of 0.8. The temperature of the experiment was in the range of  $24 \pm 2$  °C, as we aimed to highlight mesophilic microorganisms. We used the extract from leached Chernozem soil with 900-day residual crude oil contamination to inoculate microorganisms. Tatarstan crude oil high in viscosity and sulfur content was used. Substances simulating stages of microbial oil degradation—water-in-oil emulsion (Oil), glycerol (G) and oleic acid (OA)—were applied as stimulators. This approach to selecting microbes was described by Yakushev (2015). A 1:100 extraction of microorganisms from the soil was prepared according to Zenova et al. (2002). The general scheme of inoculation was the following: soil activation for 3 days—extraction—selective medium (water-in-oil emulsion/glycerol/oleic acid)—adaptation for 3 weeks—inoculation into samples. Glycerol and oleic acid had been pasteurized before incubation, but water-in-oil emulsion had not. Citrate buffer with a pH of 4 was added to the soil extract in order to inhibit bacterial growth. A drop of the extract per 15 ml of the medium was added for incubation. Three weeks later, the clays were inoculated with 10–12 drops of the selective medium per Petri dish. After fungal hyphae formed a mat on the clay surface, we sliced it and made a sandwich between two glasses creating a layer 0.5 mm thick, further called as sandwich specimen. These specimens were placed in a way to provide constant capillary contact with the water in the remaining clay and were kept for 4–5 months. After that, the sandwich specimens were taken out and slowly dried in the air. The rest of

the clay was used to prepare powder specimens to measure CA, determine the drop spreading time and for XRD analysis.

**Clay mineral composition study** was conducted by the XRD method. Before and after the microbial activity, clay samples were crushed into powder in an agate pounder with alcohol. After alcohol evaporated, they were placed into cuvettes in an air-dry state avoiding texturing for the XRD analysis. Copper radiation was applied. The exposure time was one second. The range of measurements was 0.3–40 degrees  $2\theta$ .

**Preparation of cellulose membranes for CA measurement.** The peculiarity of cellulose membranes compared to clay powders is low water absorption. Cellulose acetate is a substance similar to microbial polysaccharides, so, in this respect, it could be considered as ideal biofilm model. Two circles of the membrane Vladipor MFAC-B-1 (Russia) were placed in each clayey medium to retain hydrophobic substances, which are able to diffuse significantly during the experiment. These membranes did not allow microbial cells to go in, they weren't toxic, had 0.05  $\mu\text{m}$  of average pore diameter, 80–85% of total porosity and were 130–140  $\mu\text{m}$  thick. The membranes were kept in clays for 3, 26 and 135 days. After that, the membranes were slightly washed by distilled water to wash off ground particles, air dried and levelled under pressure. The surface of the cellulose membrane is more homogeneous than that of clay powder. However, one of the two angles in the drop projection can be smaller. Herein, the droplet asymmetry is caused by the fact that soil substances pass through membrane not as uniform flow but as fingered one. We considered the larger drop angle that formed on the membrane. There were 12 droplet measurements for each sample.

**Preparation of sandwich specimens for CA measurement.** The specimen in a wet state was carefully uncovered from one side by shifting and removing the glass, then dried at room temperature. In some cases, water vapor was absorbed by concentrated sulfuric acid in hermetic conditions. A method used for powder specimens, which is described below, was applied for settling the sessile droplets. Sandwich specimens from clays not influenced by microbes were prepared in a similar way to highlight the changes that occur on biomats.

**CA measurement on powder specimens.** Nowadays the study of wetting and drop spreading processes on soil surfaces is at a stage of choosing an appropriate method. Drop absorption and spreading time (Atanassova et al. 2018), equilibrium, quasi-stable and apparent CA (Ruíz-Cabello et al. 2014; Fer et al. 2016) as well as in situ CA obtained with non-destructive methods (Alhammedi et al. 2017) are proposed to assess hydrophilic/hydrophobic properties of clays, soils as well as a number of other porous media. We applied a methodological approach developed in recent years (Janczuk and Bialopiotrowicz 1988; Bachmann et al. 2003; Shang et al. 2008; Borysenko et al. 2009; Kholodov et al. 2015; Shein et al. 2016). The basic requirement for the compared specimens is to have the same dispersion and compaction before and after the experiment. The powder specimen is proposed to be prepared for the CA measurements by either sticking clay particles to the waterproof support (Bachmann et al. 2003) or pressing until achieving certain compaction (Arkhipov et al. 2012). We sprinkled the powder on double-sided adhesive tape,

which is glued on flat glass, and pressed at 150 Pa for 1 min. After that, non-sticky powder residues were removed by shaking once. The specimen prepared this way was placed horizontally in the focus of the USB microscope. CA was photographed from the moment when the drop separates from the pipette tip until complete spreading. The drop's volume was 25  $\mu\text{cl}$ . The pipette tip with a drop was orthogonally taken 1 mm close to the specimen's surface. Apparent CA was measured according to the first shot after drop settling (one second later) to compare with other researchers' results. In addition, the drop spreading/absorption time was determined, and then the drop's dynamics were calculated according to Eq. 1. We measured  $dr/dt$  with certain specimens' thickness  $l$  for experimental verification of this model. For this purpose, the glasses with the distributed air-dry clay powder (sample MKCP) with different layer thickness were placed in a desiccator under different vapor pressure for a week; several specimens were dried at 105 °C instead of moistening.

**Evaluation of parameters for drop spreading equation.** The drop spreading process can be investigated by observing a wet spot growing due to water film formed on the powder surface. The drop spreading rate at a fixed time relates to wet spot characteristics as:

$$\frac{dr}{dt} = \frac{a}{r} + \frac{b}{r(l + l_0)} \quad (1)$$

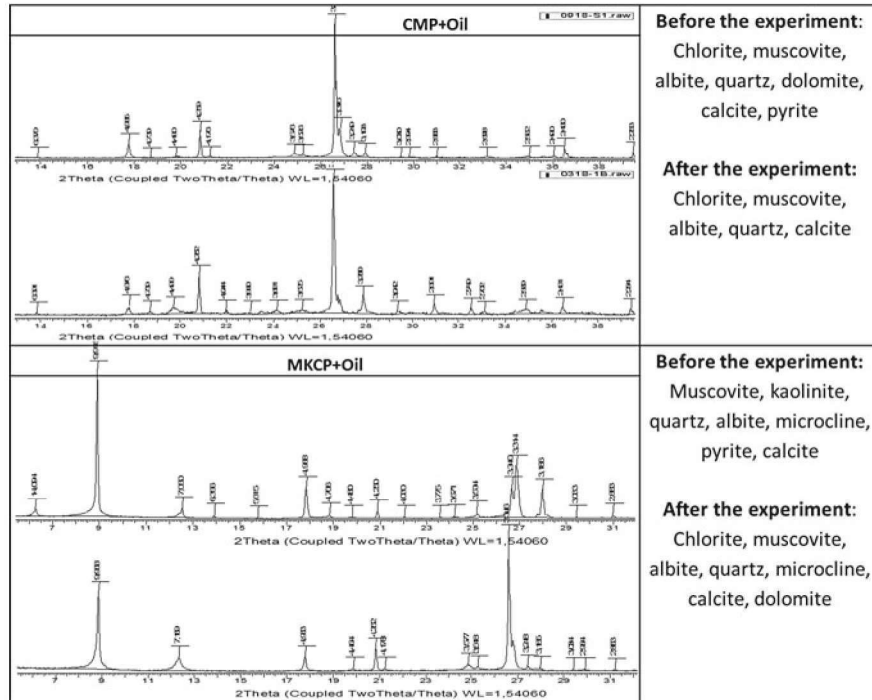
where  $r$ —spot radius;  $l$ —wet layer thickness;  $l_0$ —minimal wet layer thickness determined by grain sizes;  $a$  and  $b$  are fitting parameters involving properties of the water-solid-air system.

### 10.1.2 Results and Discussion

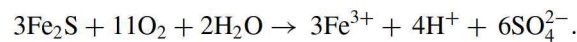
**Clay mineral composition** included:

- quartz, chlorite, muscovite—excluding sample CS;
- albite—excluding samples CS and CM;
- dolomite, calcite—excluding samples CS and LC;
- pyrite—in samples CMP and MKCP;
- microcline—in samples MKCP and LC;
- kaolinite—in sample MKCP;
- cristobalite—in sample CM.

During the experiment, there were observed changes in the composition of only two samples (Fig. 10.2). Pyrite transformed into hematite in the sample MKCP + Oil, and fine-grained (0.05–0.1 mm) pyrite in the CMP sample transformed into goethite (colloidal FeOOH). Pyrite oxidation could have both abiogenic and biogenic origin due to a highly humid environment and high oxygen availability at the same time according to the reaction (Kertesz and Frossard 2015):



**Fig. 10.2** Mineral composition of the samples



Additionally, calcite and dolomite peak heights decreased about twice with slight widening in the sample MKCP + Oil while quartz peaks remained unchanged.

**Wetting contact angles, drop spreading and absorption in clay samples.** For Eq. (1), we took  $t = 2$  and  $r = 1.8$  mm for varied wet layer thickness  $l$  (Fig. 10.3). One can see that fitted curves for partially moistured samples lie within the area limited by two curves of absolutely dry and maximal hygroscopic states of samples. It is remarkable that the exposure of clay samples without kaolinite dried in the atmosphere of sulfuric vapor for 3 weeks led to the increase in CA, i.e. increase in wetting hysteresis (Fig. 10.4). Perhaps, there was water film depletion from the surface of particles, at least, with separate spots. This, according to a theory (Summ and Gorjunov 1976), supposes overcoming the energy barrier because of the displacement of the air beneath the water droplet on a rough surface.

CA measured in our research corresponded to the definition of apparent dynamic advancing CA. As all of our surfaces in the limiting case were completely wetted, the measured CA values can be at the same time a measure of wetting hysteresis. It's necessary to stress an important point that all samples excluding CS were chemically heterogeneous like any natural disperse systems. So this heterogeneity



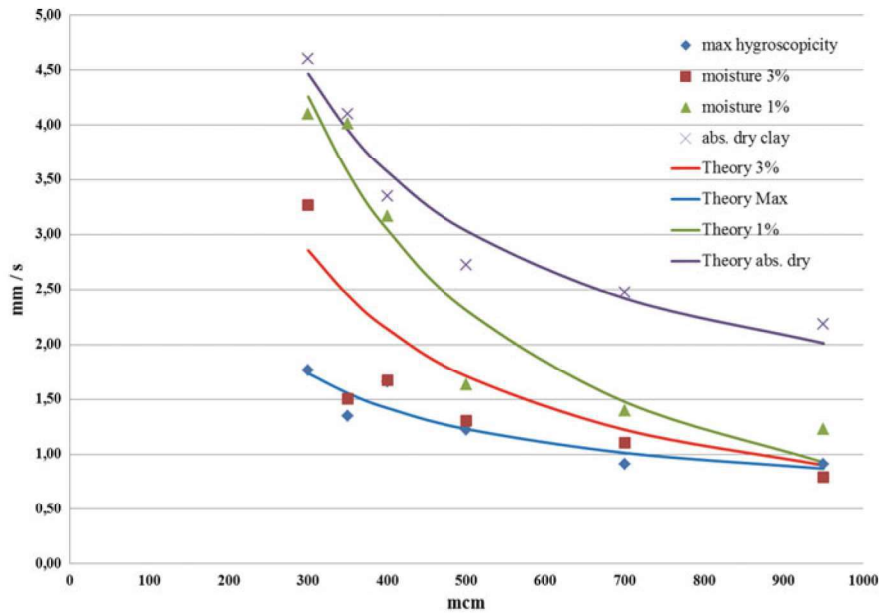


Fig. 10.3 Drop spreading rate depended on the thickness of penetrating layer. MKCP sample. The initial drop radius 1.8 mm

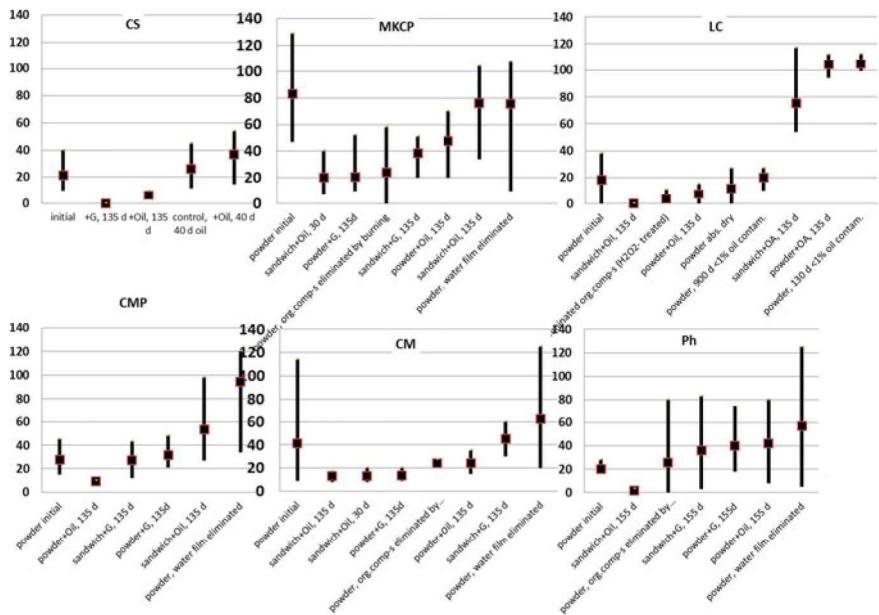


Fig. 10.4 Wetting contact angle on powder and sandwich specimens

could be expressed as a manifestation of different hydrophilic-hydrophobic properties inside the wetting line of one drop. Moreover, hydrophobic spots could appear on the hydrophilic surface after the biofilms developed, and vice versa. Therefore, such characteristics such as average, minimal, maximal CA and drop projection asymmetry are relevant for drop shape analysis.

The sample LC most expressively responded to the treatment (Fig. 10.4), and stimulated by the oleic acid, the hydrophilic surface became hydrophobic for 130 days as well as in residual crude oil contamination (<1% to weight). The sample CMP shows a weaker response to the treatment, and there was a hydrophobic transition only after water film removal. The treatment almost did not affect CA in the samples CM and CS. Meanwhile, the sample CS showed the lowest dispersion of results corresponding to its high homogeneity. The sample MKCP in its initial state possessed larger CA hysteresis compared to the other samples. Treatment of this sample either didn't change its wettability or attenuated hysteresis.

The microbial community isolated from the oil-contaminated soil successfully developed on clays when stimulating with both hydrophobic oil and hydrophilic glycerol (Fig. 10.5). The following fungi appeared on Czapek medium: *Aspergillus* sp., *Penicillium* sp., *Fusarium* sp., *Phoma* sp., *Alternaria* sp., *Mucor* sp., *Cladosporium* sp., *Trichothecium* sp. at the level of  $10^6$  CFU. The fattest biomats developed during 4–5 months on the samples CMCP + G, MKCP + G as well as LC + OA (Fig. 10.5). Hydrophilicity/hydrophobicity of the stimulator of microbial activity

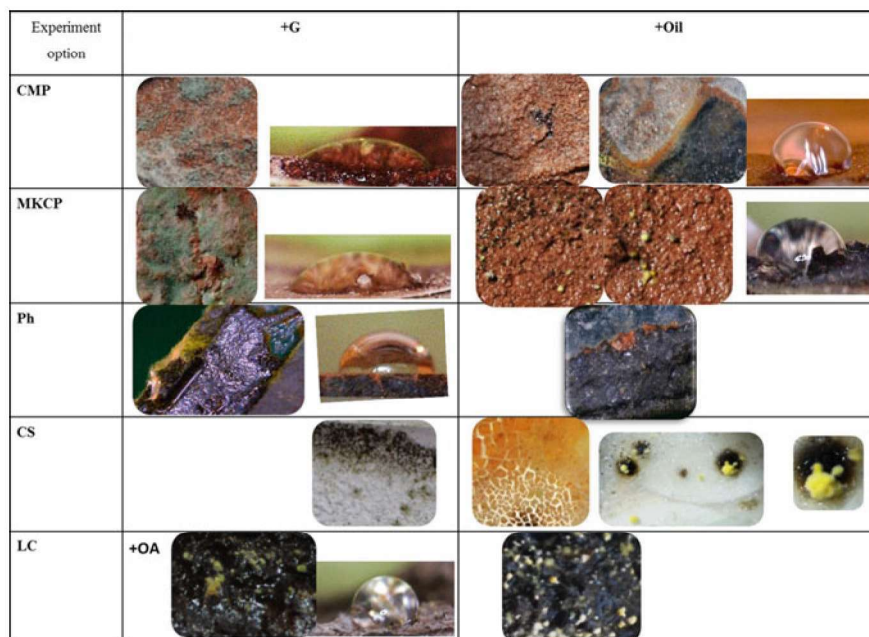


Fig. 10.5 Superficies of the samples after the experiments and drops on biomat surface

did not have a clear effect on clay properties in 135 days. The typical experimental cases are shown in Fig. 10.6: (a) wetting hysteresis was weaker in the presence of a hydrophilic stimulator than in the presence of a hydrophobic one (sample MKCP); (b) wetting hysteresis was stronger in the presence of a hydrophilic stimulator than in the presence of a hydrophobic one (sample CMP); (c) wetting hysteresis was smaller in the presence of a hydrophobic stimulator and larger in the presence of a hydrophilic stimulator than in the same sample before microbial impact (sample LC). The CA measurement demonstrated that the oil stimulation of the microbial community in the sample CS + Oil results in temporarily strong hysteresis on the 40th day, but then hysteresis disappears. However, it persists until the 155th day of the experiment in the sample Ph (Fig. 10.4). In the rest of the samples, the oil-stimulated CA hysteresis decrease was observed despite the hydrophobicity of oil. At the same time, the development of the biofilm stimulated by oil in sandwich specimens CMP + Oil and MKCP + Oil (Fig. 10.7) does not almost change their CA hysteresis, and in the case of sample Ph, the surface becomes even more hydrophilic. The fast biomat development in the sample LC + OA correlated with the CA hysteresis increase, which was like small oil contamination. The stimulation of the microbial activity with hydrophilic glycerol has an ambiguous effect on CA hysteresis: it decreases in the samples CS, CM, MKCP, increases in the sample Ph and does not change in the sample CMP. The biofilm surface after glycerol stimulation in the sample CM was more hydrophobic than the surface of this sample without any biofilm and stimulation.

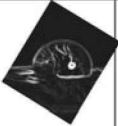


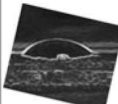

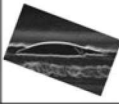

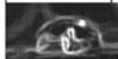
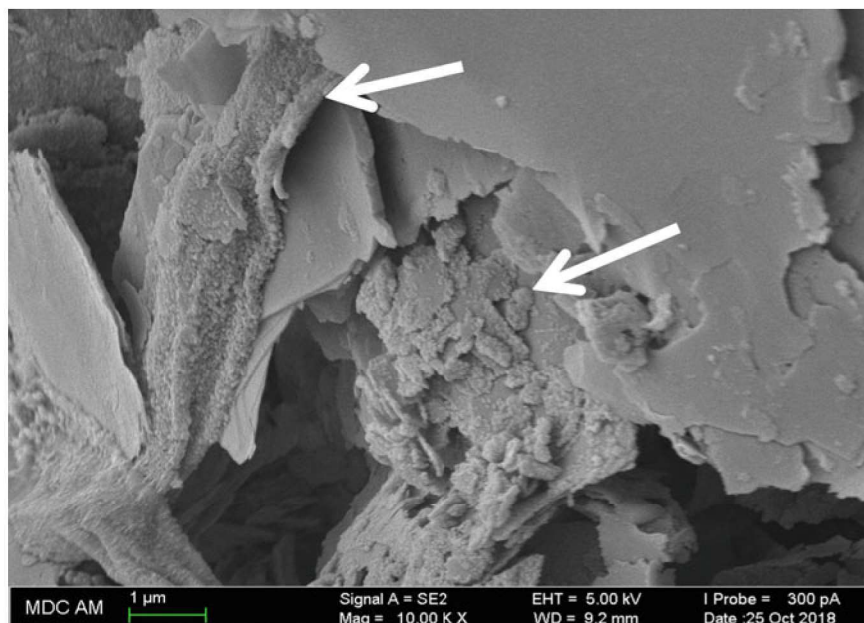
Experiment option	Initial		+G		+Oil		+OA	
	Drop shape, 1 second after seating on clay surface	Drop spreading time, s	Drop shape, 1 second after seating on clay surface	Drop spreading time, s	Drop shape, 1 second after seating on clay surface	Drop spreading time, s	Drop shape, 1 second after seating on clay surface	Drop spreading time, sec
MKCP		18		5		7	-	-
CMP		<1		9	No hysteresis	0	-	-
LC		1-3	-	-		1-2		57

Fig. 10.6 Initial drop shape on the powder surface after the microbial activity during 4–5 months



**Fig. 10.7** An example of the biofilm developed on phyllite which had been placed as a thin layer between two glasses

**CA measurement on cellulose membranes** (Fig. 10.8). The dispersion in CA values for membranes soaked in glycerol, oleic acid and water-in-oil emulsion, which are  $\pm 6^\circ$ ,  $2^\circ$  and  $6^\circ$  respectively, could be accepted as a measure of initial membrane heterogeneity. After exposing the membrane on clay surfaces, CA dispersions increased for all the specimens as a result of an increase in membrane surface heterogeneity. The sample CMP + G (the 26th day of exposure) was noticeably different from the samples with glycerol stimulation because slightly hydrophobic sites appeared alongside with sites with increased hydrophilicity compared to the initial membrane. The membrane surfaces of the samples MKCP (the 26th day of exposure) and CS (the 135th day of exposure) were subjected to hydrophilization. The results obtained on the 26th day of exposure correlate with the most abundant propagation of fungi in the samples MKCP and CMP allowing one to assume that microbial communities and/or the Fe chemical state alteration were responsible for both the hydrophilization and hydrophobization of the surface. The CA dispersion (i.e. surface heterogeneity) increased more in oil-stimulated samples than in the glycerol-stimulated ones. Moreover, this increase occurred even after a three-day exposure of the samples LC + Oil and Ph + Oil. Weakly hydrophobic sites appeared in the sample LC + Oil on the 3rd day and remained until the 135th day. Similar hydrophobic sites also appeared in the sample MKCP + Oil on the 26th day of exposure but disappeared soon. The increased hydrophilicity compared with the initial surface took place on membrane parts of the samples LC + Oil (the 26th day of exposure), CS

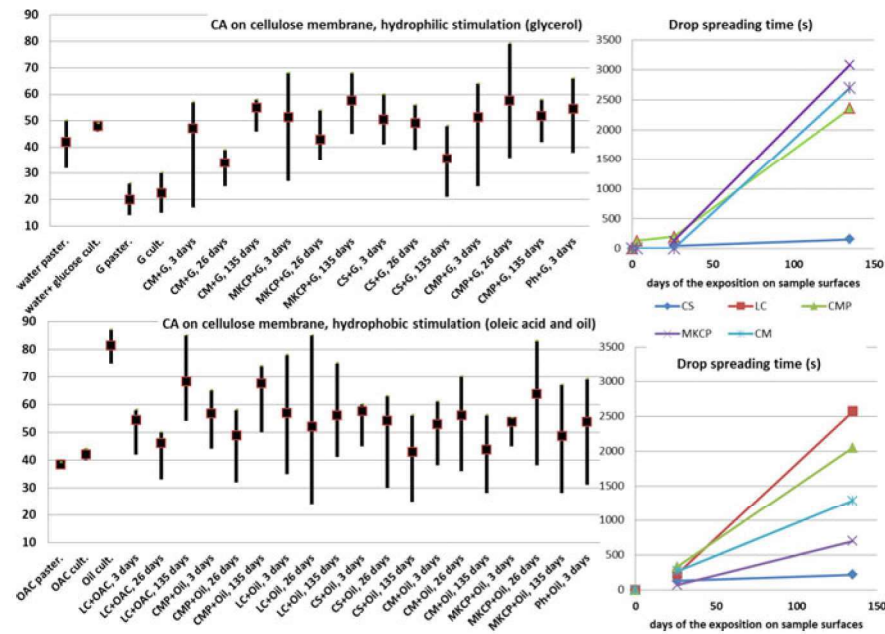


Fig. 10.8 Drop spreading onto cellulose membrane surfaces

+ Oil (from the 26th to the 135th days of exposure), CM + Oil, MKCP + Oil (to the 135th day of exposure). An increase in hydrophobicity and heterogeneity in the oleic acid-stimulated sample LC + OA was observed on the 135th day of exposure. Evidently, hydrophilic-hydrophobic properties of the membrane surface monotonically depended on the duration of exposure while the surface heterogeneity mostly increased with time. These observations comply with the assumption about the zonality of hydrophilic and hydrophobic components exudation into clays inhabited by active microorganisms. We suppose that chemicals exuded by biofilms played a key role in the surface hydrophilic-hydrophobic balance, as the number of applied stimulators was negligible. It is a wonder that the control variability range of  $\pm 6^\circ$  for CA measured in the samples stimulated by glycerol and oil exceeded in 26 out of 29 cases on membranes and in 13 out of 23 cases on powders. That is to say, the powder surface heterogeneity appeared to be lower than on the membranes despite the roughness, and chemical and geometric heterogeneity was as important as the surface hydrophilic-hydrophobic balance.

The drop spreading time was usually several hundreds or thousands of seconds on the membrane surface and less than a minute on powders. Moreover, as the experiment was carried out under atmospheric pressure, it was determined that the spreading time exceeding 5000 s could be considered as infinity compared with the evaporation time, and CA formed could be supposed as quasi-static. As the membrane saturates with compounds diffusing from soils, the drop spreading time clearly increased (Fig. 10.8). This fact proves that these compounds are partially hydropho-

bic regardless of the type of stimulation of the microbial community. Furthermore, the drop spreading time in the samples CM, CMP and MKCP increased faster in the variant with hydrophilic glycerol stimulator than with hydrophobic oil.

## 10.2 Conclusion

Relying on the results obtained one can conclude that variability in a manifestation of different hydrophilic-hydrophobic properties induced by the water and the carbon components removal and the biofilm development leads to the formation of heterogeneous spots on the surface occurred. Moreover, the water film exhausting procedure for clayey particles definitely increases the surface heterogeneity, whereas the carbon components removal and the biofilm stimulation in most cases decreases that heterogeneity for studied specimens. Clays possessed theoretically the highest initial surface energy (Chernozem soil and silica colloidal) showed the smallest dispersion in contact angle measurements. The experiment duration affected the heterogeneity spots formation non-linearly. It was found that the chemical spatial heterogeneity played a no less important role in the surface hydrophobic-hydrophilic balance than the geometrical heterogeneity. Taking into account the high sample heterogeneity (excluding silica colloidal), from the analysis of CA we can draw conclusions only about the trends in hydrophilic-hydrophobic balance alteration of samples. So, the reliable transformation from hydrophilic surface into slightly hydrophobic one took place only in case of Chernozem soil exposed to oleic acid as the stimulator for microbial growth. The chlorite-muscovite clayey sample, in which pyrite was oxidized into goethite, showed alike strong tendency towards such a transition after water film was exhausted. In rest cases, these tendencies were weaker, and only the increase in surface heterogeneity corresponding to any treatment was reliable in the sample possessed theoretically the minimal surface energy of particles (phyllite). Hydrophilic-hydrophobic properties of microbial growth stimulators did not have an unambiguous impact on contact angles. In weak biofilm cases, some recession of slight hydrophobicity occurred, perhaps, due to the microbial consumption of organic compounds and the Fe-containing components oxidizing. In fat biomat cases, the substrate hydrophobicity intensified. In the case of the apparent contact angle was about  $90^\circ$  from the beginning (muscovite-kaolinite clay), even exposed to the hydrophobic oil stimulator, the surface hydrophilization occurred. This allows us to hypothesize that the wettability of separate soil sites exposed to a number of chemicals can quickly change in any direction independently on initial hydrophilic-hydrophobic balance of a contaminant during its biodegradation. The complex influence of the clay hygroscopicity on wetting CA hysteresis was observed in the experiment. The clay moisture increasing from dry state (at  $105^\circ\text{C}$ ) to maximal hygroscopicity led to the CA hysteresis increased. However, the water film exhausting by the vapor absorption with concentrated sulfuric acid also resulted in CA increase, that is consistent with theoretical suppositions of other authors. We have been succeeded to simulate a drop spreading on the clayey powder layer of different thickness and the clay moisture ranged from dry state to maximal hygroscopicity.

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