CrossMark

NATURAL ORGANIC MATTER: CHEMISTRY, FUNCTION AND FATE IN THE ENVIRONMENT

Irreversible sorption of humic substances causes a decrease in wettability of clay surfaces as measured by a sessile drop contact angle method

Vladimir A. Kholodov[1,3] · Evgeny Y. Milanovskiy[2] · Andrey I. Konstantinov[3] ·
Zemfira N. Tyugai[2] · Nadezhda V. Yaroslavtseva[1] · Irina V. Perminova[3]

Abstract

Purpose The objective of the study was to obtain quantitative assessments of the hydrophobic impact of irreversible sorption of humic substances (HSs) onto clay mineral surfaces using a sessile drop contact angle method.

Materials and methods Two clays (kaolin and montmorillonite) were modified with four humic materials: (1) sod podzolic soil, (2) chernozem, (3) peat, and (4) coal (leonardite). The humic materials were characterized using elemental analysis, size exclusion chromatography, and ^{13}C NMR spectroscopy. Both clay samples were saturated with Ca^{2+} prior to modification with HS using a sorption isotherm technique. Contact angles (CAs) of the obtained HS-clay complexes were determined using a static sessile drop method after drying the obtained HS-clay complexes in the form of a thin film.

Results and discussion HS modification rendered both clays under study—kaolin and montmorillonite—more hydrophobic. In case of Ca-kaolin, the CA values increased from 27° (Ca-kaolin) up to 31°–32° (all HS-kaolin complexes) with no significant difference among the HS types used for modification. In the case of Ca-montmorillonite, the CA values increased from 41° (Ca-montmorillonite) up to 51°–83° with the following ascending trend for the humic types investigated: chernozem HS < coal HS < peat HS < sod-podzolic HS. This trend is in reverse to the degree of aromaticity of the HS, expressed as the content of aromatic carbon, and it is directly proportional to the molecular weight of each HS.

Conclusions Application of a sessile drop method showed increased surface hydrophobicity of HS-modified clays. Much more substantial hydrophobization was observed for montmorillonite as compared to kaolin, which was explained by the differences in the sorption mechanism.

Keywords Contact angle · Humic substances · Hydrophobization · Kaolin · Montmorillonite · Sorption · Sessile drop method

✉ Vladimir A. Kholodov
vkholod@mail.ru

Irina V. Perminova
iperm@med.chem.msu.ru

[1] Dokuchaev Soil Science Institute, Pyzhevskii Per. 7, Moscow, Russia 119017

[2] Department of Soil Science, Lomonosov Moscow State University, Leninskie Gory 1-12, Moscow, Russia 119991

[3] Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory 1-3, Moscow, Russia 119991

1 Introduction

Soil organic matter consists of up to 60–90% of humic substances (HSs). Most stable HSs in soils are incorporated into humic-clay complexes (Stevenson 1994; Laird 2001). They occur in soils, sediments, and aquifers, and it is thought that these HS are irreversibly immobilized onto clay minerals (Kononova 1966). The multiple links between molecular properties of HS and sorptive capabilities have been widely studied. For example, it has been demonstrated that the high molecular weight and low polarity of HS causes high sorption affinity to clay

🌀 Springer

minerals (Baham and Sposito 1994; Specht et al. 2000; Balcke et al. 2002; Khalaf et al. 2003; Ghosh et al. 2009). However, complexity of HS composition and large structural variations impose severe constraints on our molecular understanding of the relationships between HS structure and sorption affinities to clay minerals. As a rule, the sorption of heavy metals, actinides, and hydrophobic organic compounds by humic-clay complexes is much higher as compared to bare clay mineral surfaces (Cruz-Guzman et al. 2003; Nachtegaal and Sparks 2003; Geckeis 2004; Wang et al. 2005; Xu et al. 2006). This effect is frequently related to the substantial change in HS-modified surface properties such as hydrophobicity, surface area, and free energy (Murphy and Zachara 1995). However, quantitative estimates of these changes are very limited.

The wetting contact angle can be used as a quantitative indictor of surface hydrophobicity and free energy. It can be determined using a number of simple and quick techniques (Young 1805; Giljean et al. 2011) including the sessile drop method (both static and dynamic) (Bachmann et al. 2000), the Wilhelmy plate method, the thin-layer wicking method, and the column wicking method (Chibowski and Gonzalez-Caballero 1993). However, the contact angle of colloidal particles is difficult to measure because of small particle sizes (<2 μm in diameter), which in current methods can lead to artifacts (Shang et al. 2008; Wang et al. 2005). Clay mineral type variability can also lead to specific requirements and conditions for contact angle measurements. Contact angles for kaolin and smectite can be measured using both the static sessile drop method and the Wilhelmy plate method (Shang et al. 2008). For this study, the static sessile drop was chosen for determination of contact angles in Ca^{2+} saturated kaolin and montmorillonite and in their complexes with irreversibly sorbed HS.

The static sessile drop method has been applied primarily for smectites because these clays form a water impermeable film upon swelling. In case of kaolin, such a film contains pores and liquids can infiltrate into the pores, which decreases the contact angle (Wu 2001). Modern approaches, however, can alleviate this problem. To obtain the true contact angle for kaolin, the readings should be accomplished immediately at 0 s, before inhibition begins. The use of a digital goniometer, such as the Kruss Drop Shape Analysis System, allows for determination of the contact angle immediately after the drop is placed on the substrate, so that accurate readings at 0 s can be acquired (Shang et al. 2008).

In this study, we show the applicability of a static sessile drop contact angle method to assess wettability of both 2:1 (smectite) and 1:1 (kaolin) clays, which were modified with four humic materials isolated from soils, peat, and coal.

2 Materials and methods

2.1 Clay minerals

Kaolin clay (Kaolin CF 70) was from Caminauer Kaolinwerk GmbH (Caminau, Germany). Smectite (montmorillonite) clay was used from the bentonite deposit "10 khutor," located in Khakassia, Russia. Both clays were pretreated in the same way. Specifically, 50 mL of kaolin, at concentrations of 375 g L^{-1}, or montmorillonite, at concentrations of 150 g L^{-1}, were suspended in water and treated by an ultrasonic dispergator for 2 min (22 kHz, 0.1 kWt). The clay size particles (≤2 μm) were separated by centrifugation (at 3000 rpm for 4 min), and 1 M $CaCl_2$ was added into the supernatant until a final concentration of 0.1 M Ca^{2+} was reached. The obtained suspensions were shaken for 24 h using an overhead shaker, and then the clay particles were precipitated by centrifugation (at 3000 rpm for 5 min). The precipitate was ultrasonically redispersed in 0.001 M $CaCl_2$ at the ratio of 1:20 for kaolin and 1:40 for montmorillonite and mounted to an overhead shaker for 24 h. The procedure was repeated four times. The final suspension concentrations were stored in the dark prior to being measured gravimetrically.

2.2 Humic materials

Four humic materials were used in this study: coal (leonardite) humic acids isolated from the commercially available potassium humate (Powhumus, Humintech Ltd., Germany); peat humic acids isolated from a highmoor peat (the Tver region, Russia); soil humic acid isolated from a typical chernozem (WRB 2014) located in the Kursk region, Russia; and soil humic acid isolated from sod podzolic soil (Retisol according to WRB 2014). The samples were designated as Pow, T5, CtK06, and Pw08, respectively. The isolation protocol followed recommendations of the International Humic Substances Society (IHSS) (Swift 1996; Kholodov et al. 2015). Briefly, 1 M HCl was added to homogenized soil sample until the pH declined to 1 to 2, then the solution volume was adjusted to a final ratio of 10 mL liquid phase to 1 g of dry sample using 0.01 M HCl. The suspension obtained was shaken for 4 h and then centrifuged. The solid residue was adjusted to pH 7 using 1 M NaOH, and then 0.1 M NaOH was added until a final liquid to solid ratio of 10:1 (v/v) was reached. The suspension obtained was shaken for 4 h, left overnight, and centrifuged. The supernatant was collected and acidified using 6 M HCl to reach pH 1. The precipitate of humic acids was collected by centrifugation, redissolved in 0.1 M KOH, and then centrifuged at high speed to remove fine suspended particles. The humic acids were precipitated by acidification again, and the precipitate was treated three times with 0.1 M HCl/0.3 M HF. The treated precipitate was desalted by dialysis and brought to dryness under vacuum at 40 °C.

2.3 Structural characterization of humic materials

Elemental analyses (C, H, N) were conducted using a Vario EL analyzer. The ash content was determined by combustion in a quartz tube at 750 °C. Oxygen content was calculated as the difference between total dry weight of organic matter and the portions attributable to C, H, and N. Elemental fractions were calculated on an ash-free basis. The H/C and O/C atomic ratios were calculated as indicators of saturation degree and polarity of HS, respectively.

Size exclusion chromatography (SEC) determinations were performed as described by Perminova et al. (2003). The separations were conducted on a column packed with Toyopearl HW-55S gel (TosoHaas). Five sodium polystyrenesulfonates with known molecular weights were used for column calibration. HS solutions were set at a concentration of 10 mg L^{-1} of OC by equilibrating with the SEC mobile phase (0.028 M phosphate buffer, pH 6.8) prior to analysis. Ultraviolet (UV) absorbance at $\lambda = 254$ nm was used for detection. The number (M_n) and weight (M_w) average molecular weights and the M_w/M_n ratio (polydispersity) were calculated from these analyses.

The structural composition of HS was determined by ^{13}C NMR spectroscopy (Kovalevskii et al. 2000; Kholodov et al. 2011). An Avance 400 NMR spectrometer (Bruker) was used for acquiring the spectra after dissolving 50 mg of humic material in 0.6 mL of 0.3 M NaOD/D_2O. The spectral assignments were made as described by Hertkorn et al. (2002): 5 to 50 ppm, aliphatic H- and C-substituted C atoms (C_{Alk}); 50 to 108 ppm, aliphatic O-substituted C atoms (C_{Alk-O}); 108 to 145 ppm, aromatic H- and C-substituted C atoms (C_{Ar}); 145 to 165 ppm, aromatic O-substituted C atoms (C_{Ar-O}); 165 to 187 ppm, C atoms of carboxyl and ester groups ($C_{COO-H,R}$); and 187 to 220 ppm, C atoms of quinone and ketone groups ($C_{C=O}$).

2.4 Preparation of HS-clay complexes

HS stock solutions with concentrations of 1 and 10 g L^{-1} and containing 1 mM Ca^{2+} were used for sorption onto Ca-kaolin and Ca-montmorillonite, respectively. The HS solutions were added to clay suspensions at pH 5.5; the pH was adjusted using 0.1 M HCl and 0.1 M NaOH. The final HS concentrations were 0.5 g L^{-1} for Ca-kaolin and 4 g L^{-1} for Ca-montmorillonite. These HS concentrations were sufficient for complete saturation of all sorption sites onto kaolin and montmorillonite surfaces, based upon our preliminary experiments. The clay to HS solutions ratio was 1:80. For equilibration, the suspensions were put on an overhead shaker for 24 h and then centrifuged at 6000 rpm. The concentration of adsorbed HS was determined by measuring optical density at 465 nm before and after adsorption. To desorb reversibly bound HS from the clay-humic complexes, fresh 1 mM Ca^{2+} solution at pH 5.5 was added to the precipitate, resuspended, and shaken for 24 h. This was done six times until the optical density of desorbed HS in the supernatant equaled zero. The humic-clay complexes obtained with irreversibly adsorbed HS were kept in 0.001 M $CaCl_2$ at pH 5.5 in dark. The content of total organic carbon (OC) in the humic-clay complexes was determined and was initially 0.43% in Ca-kaolin and 0.17% in Ca-montmorillonite.

2.5 Static sessile drop method

A sessile drop method was used that has been described elsewhere (Wu 2001; Shang et al. 2008). We used a microscope slide glass (7.6 cm × 2.5 cm) that was cleaned with acetone and distilled water. The HS-clay stock suspensions at a concentration of 1–2% (by weight) were rigorously shaken for several minutes. Then, 50 µL of the suspension was placed onto the slide, left to dry for several days, and then placed in an oven at 105 °C for 2 h immediately prior to analysis. Five to seven HS-clay samples were placed onto one slide.

Contact angles were measured using a goniometer (Drop Shape Analysis System, DSA100, Kruess GmbH, Hamburg, Germany) equipped with a microsyringe steel needle. For static contact angle measurements, the microsyringe needle was positioned at 0.2 mm from the surface of the colloidal film; the volume of water drop used was 1.5 µL. The distance between the needle deposit and standby position was 1.0 mm. After dispensing, the drop shape was monitored with a digital camera for 10 s at 18 frames per second, and the contact angle was recorded. The drop contour was mathematically described by the Young–Laplace equation using DSA100 software, and the contact angle was computed as the slope of the contour line at the three-phase contact point. For each sample, a minimum 15 measurements were made, and the maximum

Table 1 Elemental composition and molecular weight characteristics of the humic materials used in this study

HS sample (source)	Elemental ratios			Molecular weight characteristics		
	H/C	O/C	C/N	M_w, kDa	M_n, kDa	M_w/M_n
T5 (peat)	1.14	0.70	26.8	19.4	1.6	12
Pw08 (sod-podzolic soil)	1.06	0.48	10.9	29.5	1.8	16.5
CtK06 (chernozem)	0.70	0.49	16.9	9.6	0.8	11.4
Pow (leonardite)	0.84	0.38	72.7	6.9	0.6	11.5

Table 2 Structural group composition of the humic materials used in this study as measured by ^{13}C NMR spectroscopy

HS sample (source)	Carbon (C) distribution among structural groups of HS, %					
	C_{Alk}	C_{AlkO}	C_{Ar}	C_{ArO}	C_{COO}	$C_{C=O}$
T5 (peat)	22	24	32	7	13	2
Pw08 (sod-podzolic soil)	24	23	20	7	16	10
CtK06 (chernozem)	9	10	44	13	19	4
Pow (leonardite)	15	7	47	12	13	5

Structural groups: C_{Alk}, aliphatic; C_{AlkO}, O-aliphatic; C_{Ar}, aromatic; C_{ArO}, O-aromatic; C_{COO}, carboxylic; $C_{C=O}$, carbonylic

number of replicates was 55. Each sampling was divided into three sub-samplings. The contact angle measurements were carried out on different days for each sub-sampling. Statistical analysis of the data obtained was performed using the software package Statistica for Windows.

3 Results and discussion

3.1 Characteristics of the humic materials used in this study

Four humic materials were used in our study for modification of clay minerals. The sources of humic materials included coal and peat, and two different soils included chernozem and sod-podzolic soil. The structural characteristics of the humic acids isolated from these sources are summarized in Tables 1 and 2.

The H/C atomic ratio in the humic materials studied varied from 0.7 to 1.14 (Table 1). An increased contribution of aromatic structures, which are reflected by lower values of H/C ratio, was observed for the coal and chernozem humic materials. The lowest O/C ratio (0.38) was observed for coal HS, whereas the highest one (0.7) was observed for peat HS. These ratios may reflect high contributions of oxygen-rich aliphatic polysaccharide structures into the molecular composition of peat HS as compared to the aromatically rich coal HS. The C/N ratio was highest in coal HS that was depleted in nitrogen. In general, the elemental compositions of the HS under study were in agreement with prior reports for similar sources (Übner et al. 2004; Tikhova et al. 2008; Kholodov et al. 2011; Mylotte et al. 2015).

Fig. 1 Sorption isotherms of coal HS onto clay minerals: **a** Ca-kaolin, **b** Ca-montmorillonite
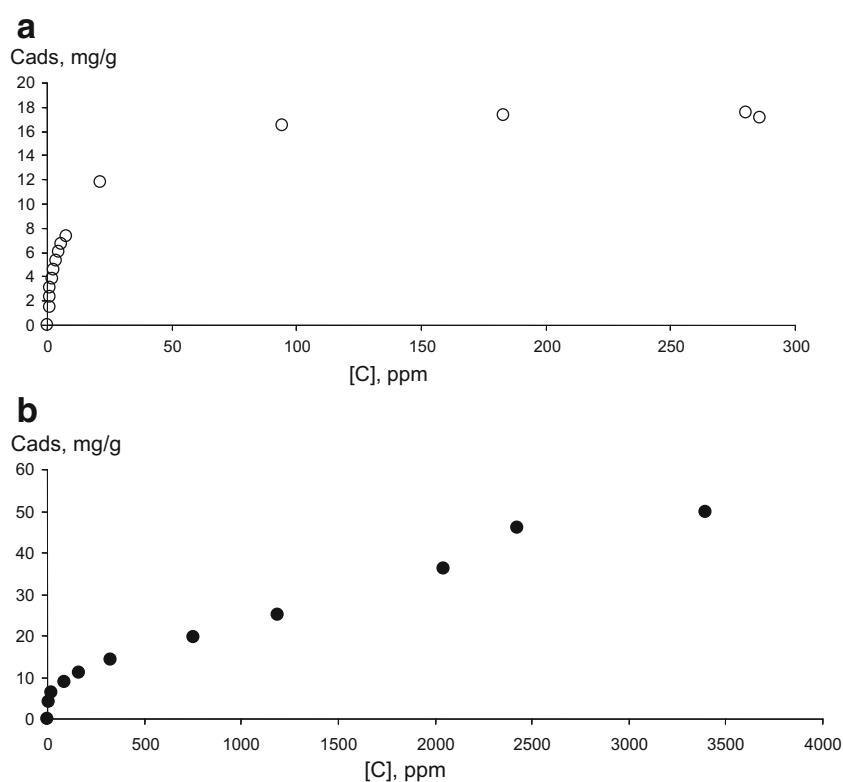
The molecular weight (M_w) characteristics of the HS samples under study are shown in Table 1. The higher M_w values were observed for peat and sod-podzolic soil HS as compared to those from coal and chernozem yielding the following ascending trend: coal < chernozem < peat < sod-podzolic soil. This is consistent with the higher content of bulky polysaccharide chains in peat and sod podzolic soil as compared to coal and chernozem HS rich in compact aromatic structures. The values obtained were also well corroborated with those reported in the literature (Perminova et al. 2003; Yuan et al. 2013).

The HS samples were analyzed using ^{13}C NMR spectroscopy in order to obtain direct evidence for structural differences. Data on the structural composition of the HS are given in Table 2. It can be seen that the highest content of aromatic carbon was observed for the coal and chernozem HS. At the same time, the sod-podzolic soil and peat HS had the highest content of heteroatom (O, N) substituted carbons, making up aliphatic moieties of carbohydrates and peptides. This is consistent with the elemental and SEC analyses for the same samples.

In summary, the data summarized above allows us to suggest that the hydrophobicity of the humic materials studied was increasing in relation to an increase in aromatic carbon content in the following order: peat < sod-podzol < chernozem ≈ coal. The humic materials could also be grouped into pairs with similar structural features: "peat–sod-podzolic soil" and "coal–chernozem soil."

3.2 Modification of clay minerals with the humic materials from different sources

The typical sorption isotherms of the humic materials on clay minerals are shown in Fig. 1. Sorption experiments demonstrated that in case of kaolin, the sorption isotherms reached a plateau at HS equilibrium concentrations ranging from 100 to 300 mg L^{-1}. In case of montmorillonite, the isotherms did not reach a plateau in the whole range of concentrations tested (up to 4000 mg L^{-1}).

To obtain the HS-clay complexes, we used the maximum HS concentration, which was 500 mg L^{-1} for Ca-kaolin and 4000 mg L^{-1} for Ca-montmorillonite. The amount of irreversibly sorbed HS on the basis of organic carbon content was as follows (% OC):

HS-Ca-kaolin: K-T5—0.69; K-Pw08—0.63; K-CtK06—1.53; K-Pow—0.92;

HS-Ca-montmorillonite: M-T5—0.67; M-Pw08—1.86; M-CtK06—1.05; and M-Pow—1.36.

There was no clear relationship between the amount of HS irreversibly sorbed onto clay minerals and their structural characteristics once sorbed to kaolin and montmorillonite. This could be due to the phenomenon of selective sorption, where only a portion of the molecular ensemble of HS is adsorbed onto a clay mineral surface.

3.3 Contact angle measurements of the different clay minerals modified with humic substances

Visual images of the water droplets obtained for the bare clays and the HS-clay complexes are shown in Fig. 2. Much steeper contact angles were observed for the montmorillonite complexes as compared to the kaolin ones. In addition, whereas the contact angles of HS complexes with Ca-kaolin were very similar to the bare clay mineral, HS-Ca-montmorillonite complexes had higher contact angles than those of non-modified clay. The corresponding contact angle values are shown in Fig. 3.

The contact angle of non-modified Ca-kaolin (K) was 27°. This value is consistent with prior reports measured by a static sessile drop method for this mineral (Shang et al. 2008). The same is true for Ca-montmorillonite (M): the contact angle of 41° was very close to the previously reported ones (Wu 2001;
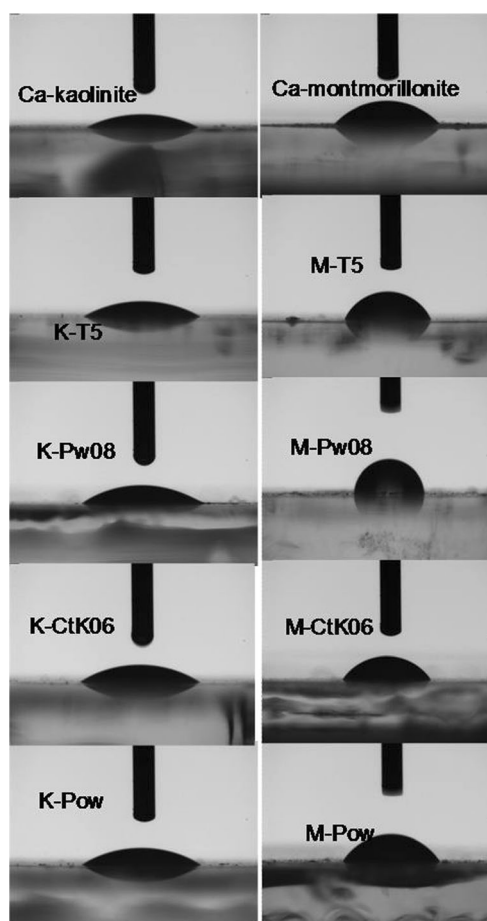
Fig. 2 Contact angles of Ca-kaolin and its HS-complexes (*left panel*): *K-T5*—peat HS, *K-Pw08*—sod-podzol soil HS, *K-CtK06*—chernozem HS, *K-Pow*—leonardite HS; Ca-montmorillonite and its HS complexes (*right panel*): *M-T5*—peat HS, *M-Pw08*—sod-podzol soil HS, *M-CtK06*—chernozem HS, *M-Pow*—leonardite HS

Fig. 3 Box whisker plots of the average contact angle values determined for the surfaces of HS-modified kaolin (**a**) and montmorillonite (**b**)
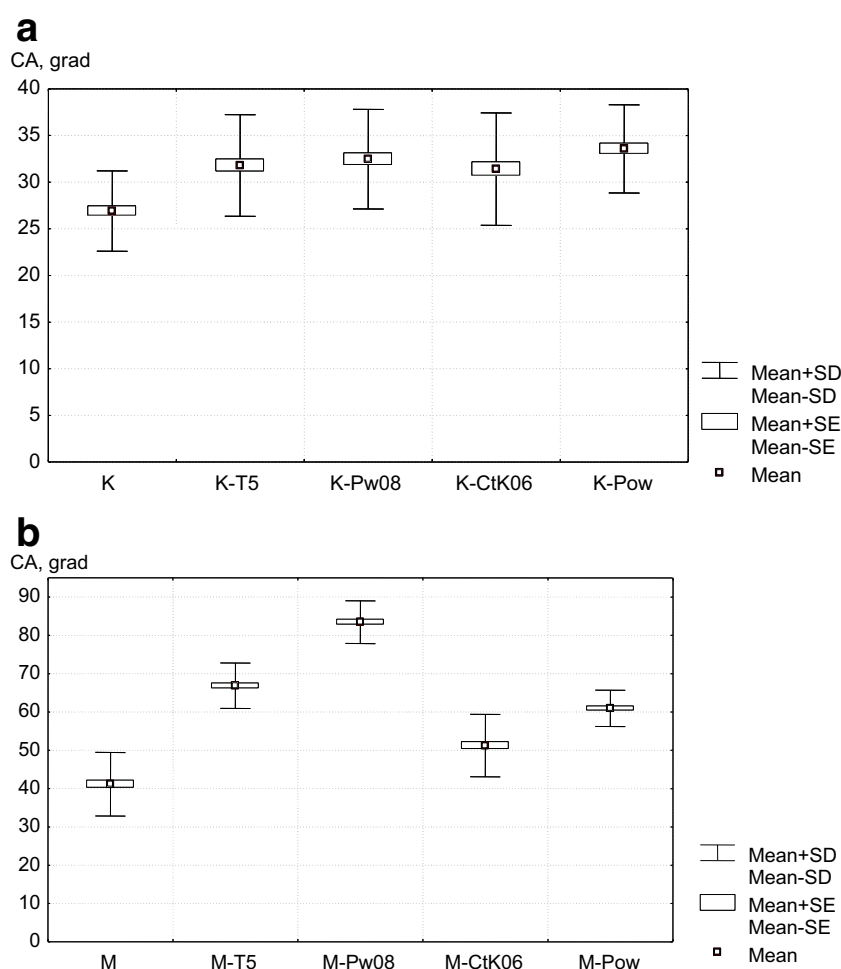

Shang et al. 2008). HS modification rendered both clays under study—kaolin and montmorillonite—more hydrophobic. In case of kaolin, this increase was very small: from 27° to 31°–32° (*t* test at $\alpha = 0.01$). We suggest that low surface area and low cation exchange capacity (Velde and Meunier 2008) might preclude strong binding of Ca-kaolin with acidic functional groups of HS via cation bridges and favor weak hydrophobic bonding between HS and Ca-kaolin surfaces. This assumption is consistent with the larger content of adsorbed HS on Ca-kaolin for more hydrophobic HS from chernozem and coal as compared to more hydrophilic HS of peat and sodpodzolic soil (Badun et al. 2009; Kulikova et al. 2010). As a result of limited modification, we did not observe relationships between the amount of HS irreversibly sorbed to Cakaolin and associated properties (Tables 1 and 2).

In case of Ca-montmorillonite, the contact angles of all HS-montmorillonite complexes were significantly larger (*t* test at $\alpha = 0.01$) as compared to Ca-kaolin, which ranged from 53° to 83°. The contact angles varied according to the following ascending trend: Ca-montmorillonite < chernozem HS-montmorillonite < coal HS-montmorillonite < peat HS-montmorillonite < sod-podzol HS-montmorillonite.

Moreover, this trend depended on the structural characteristics of the adsorbed HS. Statistically significant correlations were observed with molecular weight (M_w) and the content of aromatic carbon in the humic materials used (Fig. 4).

The higher molecular weight HS produced more hydrophobic coatings (Fig. 4a). At the same time, reverse correlations were observed for the contact angle (CA) value, based upon the hydrophobicity of HS estimated from the content of aromatic carbon (Fig. 4b). This can be explained by attachment of hydrophilic functional groups of HS (e.g., carboxyls, phenols) to positively charged surfaces of the clay mineral. This could cause a decrease in wettability of the Ca-montmorillonite-HS complexes. Moreover, at pH 5.5 in the presence of Ca^{2+}, an intermolecular aggregation of HS could occur at the surface of the clay mineral. This phenomenon becomes even more pronounced upon drying of organomineral complexes during dehydration, which can cause a change in orientation of the organic adsorbate at the clay surface (Jouany 1991), based on the surface free energy properties of the clay-organic complexes. This prior study also observed very little influence from the chemical composition of
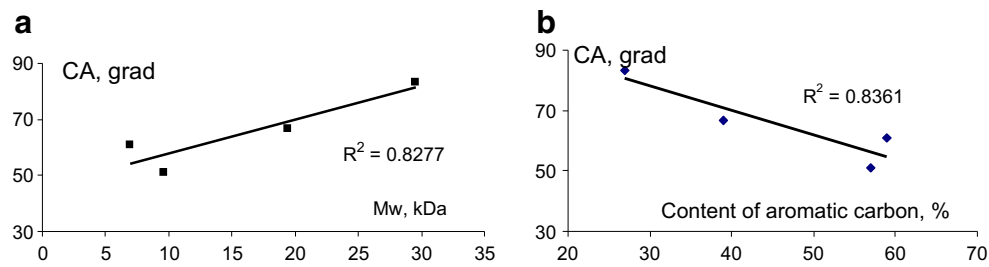
Fig. 4 Correlation of the contact angle (*CA*) of the HS-montmorillonite complexes versus molecular weight of HS (**a**) and the content of aromatic carbon (**b**) in the humic materials used

organic matter onto surface properties of organo-mineral complexes of Ca-montmorillonite.

We conducted factorial analysis of variance (factorial ANOVA) (Table 3) to determine if there are other factors contributing to the value of contact angle.

The low estimates of p values obtained in our analysis may indicate significant impacts from other factors (clay mineral and HS type) on the contact angle value based upon the F test. The estimates of effect size and power factors (e.g., partial eta-squared and non-centrality) indicate that apart from the source of HS, the clay mineral type makes a significant contribution on the contact angle value. The statistical analysis confirms that the contact angle values of HS-modified kaolin did not depend on the properties of HS, whereas for montmorillonite complexes, this dependence was much more evident.

4 Conclusions

Application of a sessile drop method demonstrated that irreversible sorption of humic substances onto surfaces of clay minerals is accompanied by a decrease in wettability or an increase in hydrophobicity. This evidence was obtained both for 1:1 (kaolin) and 2:1 (montmorillonite) clays, whereas much more substantial hydrophobization was seen with montmorillonite as compared to kaolin. At least moderate hydrophobization of the hydrophilic surfaces of clay minerals was observed with all types of humic materials used in this study (the contact angle values did not exceed 83°). This may indicate the important role of HS in sustaining soil structure via formation of water stable soil macroaggregates. Recently, Volikov et al. (2016), hypothesized that soil macroaggregates might be considered to be an inverse Pickering emulsion (i.e.,

an emulsion that is stabilized by solid particles) with water in air stabilized by clay particles that are modified by soil organic matter. This phenomenon might be similar to formation of "dry water" stabilized by hydrophobized particles of silica gels reported by Binks and Murakami (2006). The significance of wettability for water distribution and soil organic matter decomposition was demonstrated by Goebel et al. (2007). Our study provides additional arguments in favor of this hypothesis, including the theoretical rationale for the particularly beneficial effect of soil amendments capable of moderate hydrophobization of clay surfaces, e.g., mineral-adhesive HS (Volikov et al. 2016) or other humic-based hydrophobic amendments (Piccolo and Mbagwu 1999).

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

Bachmann J, Ellies A, Hartge KH (2000) Development and application of a new sessile drop method to assess soil water repellency. J Hydrol 231–232:66–75

Badun GA, Kulikova NA, Chernysheva MG, Tyasto ZA, Korobkov VI, Fedoseev VM, Tsvetkova EA, Konstantinov AI, Kudryavtsev AV, Perminova IV (2009) Tritium labeling: a unique tool for studying the behavior of humic substances in living systems. Mosc Univ Chem Bull 64(5):276–281

Baham J, Sposito G (1994) Adsorption of natural dissolved organic matter at the oxide/water interface. J Environ Qual 23:147–153

Balcke GU, Kulikova NA, Kopinke D, Perminova IV, Hesse S, Frimmel FH (2002) The influence of humic substances structure on their adsorption onto kaolin clay. SSSAJ 66:1805–1812

Binks B, Murakami R (2006) Phase inversion of particle-stabilized materials from foams to dry water. Nat Mater 5:865–869

Chibowski E, Gonzalez-Caballero F (1993) Theory and practice of thin-layer wicking. Langmuir 9(1):330–340

Table 3 Univariate tests of significance, effect sizes, and powers for contact angles

Factor	F	p	Partial eta-squared	Non-centrality
Clay mineral	1654	0.000	0.843	1654
HS	140	0.000	0.644	559
HS-clay complexes	84	0.000	0.520	335

Over-parameterized model type III decomposition

Cruz-Guzman M, Celis R, Hermosin MC, Leone P, Negre M, Cornejo J (2003) Sorption-desorption of lead (II) and mercury (II) by model associations of soil colloids. Soil Sci Soc Am J 67:1378–1387

Ghosh S, Zhen-Yu W, Kang S, Bhowmik PC, Xing BS (2009) Sorption and fractionation of a peat derived humic acid by kaolinite, montmorillonite, and goethite. Pedosphere 19(1):21–30

Giljean S, Bigerelle M, Anselme K, Haidara H (2011) New insights on contact angle/roughness dependence on high surface energy materials. Appl Surf Sci 257(22):9631–9638

Geckeis H (2004) Colloid influence on the radionuclide migration from a nuclear waste repository. Geol Soc Lond, Spec Publ 236:529–543

Goebel MO, Woche SK, Bachmann J, Lamparter A, Fischer WR (2007) Significance of wettability-induced changes in microscopic water distribution for soil organic matter decomposition. Soil Sci Soc Am J 71:1593–1599

Hertkorn N, Permin AB, Perminova IV, Kovalevskii DV, Yudov MV, Kettrup A (2002) Comparative analysis of partial structures of a peat humic and fulvic acid using one and two dimensional nuclear magnetic resonance spectroscopy. J Environ Qual 31:375–387

Jouany C (1991) Surface free energy components of clay-synthetic humic acid complexes from contact-angle measurements. Clay Clay Miner 39(1):43–49

Khalaf M, Kohl SD, Klumpp E, Rice JA, Tombacz E (2003) Comparison of sorption domains in molecular weight fractions of a soil humic acid using solid state ^{19}F NMR. Environ Sci Technol 37:2855–2860

Kholodov VA, Yaroslavtseva NV, Konstantinov AI, Perminova IV (2015) Preparative yield and properties of humic acids obtained by sequential alkaline extractions. Eurasian Soil Sci 48(10):1101–1109

Kholodov VA, Konstantinov AI, Kudryavtsev AV, Perminova IV (2011) Structure of humic acids in zonal soils from ^{13}C NMR data. Eurasian Soil Sci 44(9):976–983

Kovalevskii DV, Permin AB, Perminova IV, Petrosyan VS (2000) Conditions for acquiring quantitative ^{13}C NMR spectra of humic substances. Mosc Univ Chem Bull 41:39–42

Kononova MM (1966) Soil organic matter its nature, its role in soil formation and in soil fertility, 2nd ed.; Pergamon Press, Ltd: Oxford, London, Edinburgh, New York, Toronto, Sydney, Paris, Braunschweig

Kulikova NA, Perminova IV, Badun GA, Chernysheva MG, Koroleva OV, Tsvetkova EA (2010) Estimation of uptake of humic substances from different sources by Escherichia coli cells under optimum and salt stress conditions by use of tritium-labeled humic materials. Appl Environ Microbiol 76(18):6223–6230

Laird D (2001) Nature of clay–humic complexes in an agricultural soil: II. Scanning electron microscopy analysis. Soil Sci Soc Am J 65:1419–1425

Mylotte R, Verheyen V, Reynolds A, Dalton C, Patti AF, Chang RR, Burdon J, Hayes MHB (2015) Isolation and characterisation of recalcitrant organic components from an estuarine sediment core. J Soils Sediments 15(1):211–224

Murphy EM, Zachara JM (1995) The role of sorbed humic substances on the distribution of organic and inorganic contaminants in groundwater. Geoderma 67:103–124

Nachtegaal M, Sparks DL (2003) Nickel sequestration in a kaolinite-humic acid complex. Environ Sci Technol 37:529–534

Perminova IV, Frimmel FH, Kudryavtsev AV, Kulikova NA, Abbt-Braun G, Hesse S, Petrosyan VS (2003) Molecular weight characteristics of humic substances from different environments as determined by size exclusion chromatography and their statistical evaluation. Environ Sci Technol 37:2477–2485

Piccolo A, Mbagwu JSC (1999) Role of hydrophobic components of soil organic matter in soil aggregate stability. Soil Sci Soc Am J 63: 1801–1810

Specht CH, Kumke MU, Frimmel FH (2000) Characterization of NOM adsorption to clay minerals by size exclusion chromatography. Water Res 34:4063–4069

Shang J, Flurya M, Harsha JB, Zollars RL (2008) Comparison of different methods to measure contact angles of soil colloids. J Colloidal Interface Science 328:299–307

Swift RS (1996) Organic matter characterization (chap 35). Methods of soil analysis. Madison, WI: Soil Science Society of America, Part 3. 1018–1020

Stevenson FJ (1994) Humus chemistry: genesis, composition, and reactions, 2nd edn. Wiley, New York

Tikhova VD, Fadeeva VP, Dergacheva MI, Shakirov MM (2008) Analysis of humic acids from various soils using acid hydrolysis. Russian. J Appl Chem 81(11):1957–1962

Übner M, Treuman M, Viitak A, Lopp M (2004) Properties of humic substances from the Baltic Sea and Lake Ermistu mud. J Soils Sediments 4(1):24–29

Velde B, Meunier A (2008) The origin of clay minerals in soils and weathered rocks. Publisher Springer Berlin Heidelberg. doi:10.1007/978-3-540-75634-7. 406 pp

Volikov AB, Kholodov VA, Kulikova NA, Philippova OI, Ponomarenko SA, Lasareva EV, Parfyonova AM, Hatfield K, Perminova IV (2016) Silanized humic substances act as hydrophobic modifiers of soil separates inducing formation of water-stable aggregates in soils. Catena 137:229–236

Wang H-W, Dong R-X, Chu H-C, Chang K-C, Lee W-C (2005) Improvements on the synthesis and properties of fluorinated polyimide-clay nanocomposites by using double swelling agents. Mater Chem Phys 94:42–51

Wu W (2001) Baseline studies of the clay minerals society source clays: colloid and surface phenomena. Clays Clays Min 49(5):446–452

Xu D, Wang XK, Chen CL, Zhou X, Tan XL (2006) Influence of soil humic acid and fulvic acid on sorption of thorium(IV) on MX-80 bentonite. Radiochim Acta 94:429–434

World reference base for soil resources (2014) A framework for international classification, correlation and communication, Word Soil Resourse Report 106. FAO. Rome. 2014. 181 pp

Young T (1805) An essay on the cohesion of fluids. Philos Trans R Soc Lond 95:65–87

Yuan Y, Zhou S, Yuan T, Zhuang L, Li F (2013) Molecular weight-dependent electron transfer capacities of dissolved organic matter derived from sewage sludge compost. J Soils Sediments 13(1):56–63