

**Doctoral (Ph.D.) theses**

**Interfacial and colloid interactions in complex  
aqueous disperse systems containing  
montmorillonite, iron oxide, humic acids and  
calcium ions**

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## 1. Introduction

Soil is a three-phase complex system, which contains inorganic (43-45%) and organic (5-7%) solids, air (5-20%) and water (30-45%). Their ratio depends on the quality of the soil specimen. The solid part of soil includes organic **humic substances** and polysaccharides of colloid size. The mineral components of small particle sizes ( $< 2 \mu\text{m}$ ) constitute the class of clay fractions, which are composed of silicates, **clay minerals**, **oxides**, hydroxides, carbonates, sulphides and chlorides. The most relevant parts of the clay fraction are the **clay minerals**. Owing to their adsorption and ion-exchange properties, they play a significant role in the control of soil processes and the interaction between the water and the solid phase.

Since **iron oxide** particles of colloid dimensions greatly influence the structure of the soil, hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ) were chosen for the investigations modeling the aggregation of the particles that build up the soil structure. Magnetite bears a specific importance due to its magnetic property. It has a wide range of applications in the industry and electronic devices (e.g. magnetic fluids in HiFi devices) and its medical applications have also been reported recently. Hematite has been used as a dye since the antiquity due to its characteristic red colour.

**Humic substances** are mixtures of macromolecular materials, predominantly with acidic character. They form during the physicochemical and microbiological degradation of vegetal and animal residues, and they can be found in the soil and surface waters as well as groundwaters in dissolved or precipitated form. These organic macromolecules with a great variety of chemical structure and good complexation properties possess many beneficial effects, e.g. they increase the fertility of soils, but human consumption of the metal complexes of humates is also known. It is disadvantageous, though, that their interaction with organic and metal contaminants increases their solubility (via solubilization of e.g. hydrophobic pesticides and complexation of e.g. copper or radioactive isotopes) causing therefore serious environmental problems.

Humic substances are bound to mineral particles in the soil. Their coating results in the formation of an organically modified surface, the charge properties and aggregation behaviour of which differs from those of "pure" mineral components. Thus, the interaction between mineral particles and the dissolved and dispersed species of the soil solutions is also affected. Therefore, humic substances play a dominant role in the environmental processes. When the pH of the soil exceeds the value of 6, humic substances are present as polyanions. Their negatively charged functional groups repel the negatively charged lamellar

surfaces of the clay minerals; connection between them is therefore only possible through the Al-OH edge sites by complex bond formation. Furthermore, as the soil contains different structure-forming ions such as  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$ , the organic and inorganic components can be linked through cation bridges. Consequently, these ions (especially  $\text{Ca}^{2+}$ ) influence the structure, crumbliness and quality of the soil.

The interfacial and colloidal interactions and their relationship were studied in model systems containing the soil constituents montmorillonite, humic acid, iron oxides and calcium, which have a definite role in the formation of soil structure. Materials synthesized in laboratory conditions were used in soil relevant composition to get a better understanding of the processes in the soils (structure building and structure improvement).

The objectives of the present work are as follows:

to investigate the dissociation and ion distribution processes of humic acid extracted from peat and Na-montmorillonite separated from bentonite. The effect of calcium ions on humic acid, and the ionic strength and pH dependent charge state of hematite and magnetite particles by means of potentiometric acid-base titration are also considered.

to synthesize the magnetite and hematite nanoparticles and to characterize them by means of X-ray diffraction (XRD),  $\text{N}_2$  adsorption and transmission electron microscopy (TEM).

to study the adsorption of humic acid on montmorillonite and montmorillonite/iron-oxide composites in the presence of  $\text{Ca}^{2+}$ .

to investigate the fractionation of humic acids upon their adsorption.

to determine the amount of dissolved, adsorbed (bound to the solid phase) and complexed (by the humic acid) calcium ions by means of calcium ion selective electrode and titration with a specific complexation agent, EGTA.

to study the charge properties of humic acid, Na-montmorillonite, magnetite and hematite particles and those of their binary and ternary systems.

to investigate the dispersing and aggregating effect of humic acid (HA) and calcium salt addition by means of rheology and to get information on the formed structure by means of scanning and transmission electron microscope (SEM and TEM) pictures.

## 2. Materials and methods

Montmorillonite was obtained from Wyoming bentonite by sedimentation. HA was extracted from peat using the standard method of the International Humic Substances Society. Magnetite and hematite was synthesized in alkaline hydrolysis of concentrated  $\text{FeCl}_2$  and  $\text{FeCl}_3$  solutions and  $\text{FeCl}_3/\text{HCl}$  solution, respectively. Chemicals of analytical purity (obtained from Reanal) were used for the experiments. Measurements were performed on room temperature ( $25 \pm 1$  °C) and atmospheric pressure.

The synthesized iron oxides were characterized by X-ray diffraction (**XRD**), Philips X-ray diffractometer (PW 1830 generator, PW 1820 goniometer,  $\text{CuK}\alpha$  radiation:  $\lambda = 0,1542$  nm, 40kV, 25 mA) was used), **N<sub>2</sub> adsorption** (BET method was used to evaluate the results) and transmission electron microscopy (**TEM**).

Specific surface area of the lyophilized (freeze dried) magnetite and hematite samples was determined by Gemini 2375 gas adsorption apparatus produced by Micrometrics.

Size analysis of iron-oxide nanoparticles was carried out in a Philips CM-10 transmission electron microscope at an acceleration voltage of 100 kV. Electron micrographs were recorded by a Megaview-II digital camera attached to the instrument. Average particle diameters and size distribution functions were determined using the UTHSCSA Image Tool software at the Department of Pathology.

The pH-dependent equilibria, the simultaneous  $\text{H}^+$  exchange of montmorillonite and the protonation and deprotonation processes of their Al-OH sites, as well as Fe-OH sites of iron-oxides, and dissociation of acidic groups of humic acids were investigated by potentiometric **acid-base titration**. The titration apparatus (GIMET1) was made in our department controlled by computer.

The influence of added  $\text{Ca}^{2+}$  ions on the **HA adsorption** was investigated in NaMt and mixed NaMt/Mag, NaMt/Hem (30:1) suspensions, respectively, to reveal the interactions of ionic and molecular species with solid particles in composite systems. The adsorption series were measured at pH ~6.5 and ~0.01 M NaCl after 1 day adsorption time. The equilibrium supernatants were analyzed, the adsorbed amount of HA was determined by means of UV-VIS spectra (UVIKON 930) and the total calcium content (all free and HA bound  $\text{Ca}^{2+}$  in the solution phase) by titration with EGTA.

The influence of HA and calcium salt addition to the mixed suspensions on the charge state of solid particles and the change in the pH-dependent charge state of iron oxides after HA and HA and  $\text{Ca}^{2+}$  addition was characterized by **zeta potential measurement** with ZetaSizer 4 instrument (Malvern, U.K.) at  $25 \pm 0.1$  °C.

The dispersing-aggregating effect of HA and calcium salt addition was measured by means of rheology (RS150 rheometer, HAAKE), cone-plate sensor (DC60/2° Ti), at 25±0.1°C and Reowin softwer. At the structure building measurements, the ratio of solid components (montmorillonite/iron oxide) was 24:1, at pH ~6.5 and 10 mM NaCl.

The composite suspensions containing montmorillonite, humic acid, iron oxide and calcium ions were investigated by means of scanning electron microscope (SEM, Hitachi S-4700 at the Department of Applied and Environmental Chemistry) to present formed lamellae structure.

### **3. New scientific results**

#### *T.1 Spontaneous transformation of magnetite upon prolonged storage.*

The X-ray diffraction (XRD) of magnetite proved that a solid phase transformation took place during longer storage, maghemite and akagenite shell on magnetic core formed. A slight increase in particle size was observed after storage as well. The recrystallization resulted in a significant decrease in the specific surface area of the aged sample. The specific surface area of aged magnetite was about one quarter (~27 m<sup>2</sup>/g) of the fresh sample (95,35 m<sup>2</sup>/g). The potentiometric acid-base titration and zeta-potential measurements of magnetite, which was stored in acidic suspension for several years, revealed that the pH<sub>pzc</sub> and pH<sub>iep</sub> values decreased from pH~8 to ~7.

#### *T.2 Titration results of humic acid with Ca<sup>2+</sup> ions.*

The interaction of humic acid with Ca<sup>2+</sup> ions was studied by potentiometric titration. This investigation showed a difference between the effect of indifferent ion (Na<sup>+</sup>) and Ca<sup>2+</sup> as divalent specific ion. The higher the Ca<sup>2+</sup> loading in the HA solution is, the higher the net proton surface excess is; that is, H<sup>+</sup> ions from acidic functional groups of humic acid were released in the presence of Ca<sup>2+</sup> ions.

#### *T.3 Adsorption results of humic acid and Ca<sup>2+</sup> ions on Na-montmorillonite, and on mixed Na-montmorillonite/magnetite, Na-montmorillonite/hematite.*

3.a Adsorption of humic acid and calcium ions on Na-montmorillonite and on the mixture of Na-montmorillonite and iron-oxides (magnetite and hematite) showed that the amount of adsorbed HA increased with increasing HA concentration at constant Ca<sup>2+</sup> concentration. The adsorbed HA amounts increased significantly in the adsorption series measured at different Ca loadings. HA can be bound through Ca-bridges between its acidic, mainly carboxylic groups and lamellae of montmorillonite. The permanent negative

charges on the face of montmorillonite lamellae provide the sites for cation exchange, where  $\text{Ca}^{2+}$  ions can be bound and pH-dependent charges can develop on the amphoteric sites, mainly  $\text{Al-OH}$  groups at edges. Humate polyanions are bound through Ca-bridges and by surface complexation on  $\text{Al-OH}$  sites of montmorillonite and on  $\text{Fe-OH}$  sites in mixed suspensions containing iron oxides. In the case of the samples containing only montmorillonite the specific enhancing effect of  $\text{Ca}^{2+}$  became characteristic only at the highest Ca loadings (5.5 mM, which is 100 % of CEC of montmorillonite), where enough  $\text{Ca}^{2+}$  was present to form binding sites for HA even in the second layer of adsorption on montmorillonite surface.

3.b The shape of adsorption isotherms of HA measured in the clay suspensions containing the same amounts of magnetite and hematite, were similar and the amounts of adsorbed HA were not significantly different due to the similar specific surface area of the iron oxides. The mixed adsorbents both the Na-montmorillonite/hematite and the Na-montmorillonite/magnetite adsorbed double amount of HA compared with the samples containing only montmorillonite at lower  $\text{Ca}^{2+}$  (25, 50%) loadings. Although the adsorption capacity of mixed adsorbents were still greater, the difference was already smaller at 75%  $\text{Ca}^{2+}$ , however, slightly less HA was adsorbed on the mixed adsorbents than that on pure clay at the highest (100 %)  $\text{Ca}^{2+}$  content. The reason of decreasing capacity of HA adsorption presumably is that the positively charged iron oxide nanoparticles occupy the cation exchange sites on the face of montmorillonite lamellae from before  $\text{Ca}^{2+}$  ions. It is supported by the fact that the adsorbed amount of  $\text{Ca}^{2+}$  ions is about 20 % smaller in the samples containing iron oxides than that in pure montmorillonite suspensions. This result showed a competition between positively charged nanoparticles and exchangeable  $\text{Ca}^{2+}$  cations for negative surface sites.

3.c. Solid/liquid (S/L) distribution of  $\text{Ca}^{2+}$  was attempted to be measured by using a  $\text{Ca}^{2+}$  ion selective electrode (ISE). The ISE method is not applicable for the determination of free  $\text{Ca}^{2+}$  ion in the presence of HA because of its probable chemical interference with the ISE membrane.

3.d. The total  $\text{Ca}^{2+}$  concentration (free and bound to HA) was measured in the equilibrium solution phase by means of titration with EGTA. It can be concluded that the adsorption of calcium increases gradually with increasing  $\text{Ca}^{2+}$  content. Less amount of  $\text{Ca}^{2+}$  is adsorbed on the mixed adsorbents than on pure Na-montmorillonite probably due to the reduction of the number of cation exchange sites, since these negative surface sites on montmorillonite lamellae are occupied in part by iron oxide nanoparticles carrying positive charges at  $\text{pH}\sim 6.5$ . The adsorption of calcium and HA increases gradually with increasing  $\text{Ca}^{2+}$  content but different degree. The fourfold increase in  $\text{Ca}^{2+}$  loading resulted in more than a tenfold increase in HA adsorption, but  $\text{Ca}^{2+}$  adsorption was only three times greater. At the lowest Ca loading,  $\sim 90$  % of the  $\text{Ca}^{2+}$  ions were

accumulated in the solid phase, however, the ratio of  $\text{Ca}^{2+}$  interfacial distribution decreased with increasing  $\text{Ca}^{2+}$  concentration.

3.e. The adsorptive fractionation of HA was tested in adsorption series containing  $\text{Ca}^{2+}$ . The values of the specific adsorption  $\text{SUVA}_{254}$  (in connection with the aromaticity of HA samples),  $E_3/E_4$  and  $E_4/E_6$  ratios (having inverse relationship with the humification degree and size of molecules) were calculated from the spectra of the supernatants and compared with that of HA solutions having similar ionic composition. The spectral parameters were higher in the Ca-rich supernatants, so less aromatic and larger fractions were bound to both pure montmorillonite and its mixture with hematite and magnetite particles.

#### *T.4 The results of zeta-potential measurements.*

4.a The dominance of permanent negative charges on montmorillonite and the presence of dissociated acidic groups of HA particles were obvious from the negative zeta-potential values observed over the whole range of  $\text{Ca}^{2+}$  concentration. There is an increase in zeta-potential, which is especially significant for HA due to the reaction with  $\text{Ca}^{2+}$ , however, calcium addition cannot induce the zeta-potential reversal of these highly charged particles, even if applied in great excess. The zeta potential values of ternary (Na-Mt/  $\text{Ca}^{2+}$ /HA) system did not show significant change.

4.b Zeta-potential of magnetite and hematite were positive at pH~6,5 and 10 mM NaCl concentration, and it became negative (this phenomenon is termed as zeta-potential reversal) even at low HA loading, because the increasing amount of HA was capable for covering iron oxide particles first in part neutralizing the positive charges on the surface of iron oxides, then completely overcharging their surface. In the presence of  $\text{Ca}^{2+}$ , only negative potential values were measured in systems containing HA covered iron oxide particles similarly to the Na-montmorillonite suspensions.

#### *T.5 Investigation on the dispersing/aggregating effect of $\text{Ca}^{2+}$ and HA in Na-montmorillonite, Na-montmorillonite/magnetite and Na-montmorillonite/hematite suspensions.*

5.a The rheological investigation of relative dense suspensions of pure Na-montmorillonite as well as their mixtures containing either hematite or magnetite in a mass ratio of 24:1 showed that the lamellae of montmorillonite could form a loose network at pH ~6,5 and 6,6 mM NaCl due to the electrostatic attraction between negatively charged faces and positively charged surfaces both on edges and oxide particles. The network formed in the mixed montmorillonite and iron oxides suspensions is stronger. This aggregated structure cannot form above a given HA concentration because the Al-OH sites at the edges and Fe-OH sites on the iron oxide surfaces are completely covered by the functional

groups of HA. Calcium addition, even a very small amount, causes an obvious change in flow behavior. With increasing Ca loading, a definite plastic character and larger and larger thixotropic loops appear. A strong attractive gel can form at the greater  $\text{Ca}^{2+}$  loadings. The semi-solid particle network formed in suspensions containing 6.67 mM and 13.3 mM  $\text{Ca}^{2+}$  can be broken down by increasing HA loading, the liquefying effect of HA depends on the concentration of  $\text{Ca}^{2+}$  ions. There was no essential difference between the behaviour of pure montmorillonite suspension and its mixture with iron oxides.

5.b Modeling of soil conditions was attempted by studying suspensions with the composition of the colloid fraction of organic-rich and organic-poor soils. It was observed both in the presence of iron oxides (either magnetite or hematite) and in their absence that the dispersing effect of organic matter, here HA, can be eliminated with Ca addition in appropriate amounts. In general, the greater the organic matter content is, the larger the expected Ca loading is. A significant strengthening of the clay particle network can be reached at higher organic matter content, if enough Ca is also present, first to bind the organic anions to the clay surface and then to bridge the organic matter coated clay plates.

5.c To estimate how much  $\text{Ca}^{2+}$  is enough, it is worth taking into account the charged species, the negative charges of montmorillonite and the acidic groups in HA, which should be neutralized by  $\text{Ca}^{2+}$ . Observations showed that liquefaction under the charge balance and solidification above it was expected. The amount of  $\text{Ca}^{2+}$  to induce charge reversal is in accordance with  $\text{Ca}^{2+}$  concentration where it is significant to solidify the suspensions. In iron oxide containing systems, owing to the presence of positive surface sites  $\text{Fe-OH}_2^+$ , less  $\text{Ca}^{2+}$  is needed to neutralize the charges.

It is worth taking into account the balance of oppositely charged species in clay suspensions with variable organic matter content to estimate an optimal Ca loading for their significant solidification. It is supposed that this charge balance concept may be useful for predicting the strengthening of clay suspensions and to differentiate the nature in interactions.



#### 4. Publications related to the scientific topic of the dissertation

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2. E. Tombácz, **A. Majzik**, Zs. Horváth, E. Illés: Magnetite in aqueous medium: coating its surface and coated with it  
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3. **A. Majzik**, E. Tombácz: Interactions between humic acid and montmorillonite in the presence of calcium ions I. Interfacial and aqueous phase equilibria: adsorption and complexation  
*Organic Geochem.* 38: 1319-1329 (2007)  
IF<sub>2006</sub>: **2,331**
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5. E. Tombácz, E. Illés, **A. Majzik**, A. Hajdú, M. Szekeres, Ageing in inorganic nanoworld: an example for magnetite nanoparticles in aqueous medium,  
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6. E. Tombácz, D. Bica, A. Hajdú, E. Illés, **A. Majzik**, L. Vékás: Surfactant double layer stabilized magnetic nanofluids for biomedical application,  
*Journal of Physics - Condensed Matter* (submitted)  
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**Σ IF: 9,374**

## Lectures and posters in Hungarian and International conferences

### Proceedings

1. E. Tombácz, E. Illés, **A. Majzik**: *Humic acid adsorption on oxides: a meaningful comparison of data* In: Humic Substances and Soil and Water Environment (Eds. L. Martino-Neto et al.) Proc. 12<sup>th</sup> International Conference of International Humic Substances Society, Embrapa, Sao Pedro, Sao Paulo, Brazil, 2004. pp. 52-54.
2. **A. Majzik**, E. Tombácz: *Elastic network of lamellar particles formation and rheological characterization*, Rheofuture Conference, July 1-2, Karlsruhe, Germany, 2004,  
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3. **A. Majzik**, E. Tombácz: *Joint effect of humic acids and calcium ions on particle interactions in composite aqueous suspensions of clay and iron oxides*, poster, lecture in 3 min, Proc. 13<sup>th</sup> International Conference of International Humic Substances Society, July 30-Aug 4, Karlsruhe, Germany, 2006. pp. 705-708.

### Abstracts

4. **A. Majzik**, E. Tombácz: *Elastic network of lamellar particles formation and rheological characterization*, poster, 2<sup>nd</sup> Mid-European Clay Conference, Sept 20-25, 2004. Miskolc, Hungary, Acta Mineralogica-Petrographica Abstract Series 4, Szeged, 2004. p.70.
5. **Majzik A.**, Tombácz E.: *Interfacial and colloidal interactions in soil modeling complex systems*, lecture, The VIII<sup>th</sup> International Symposium Romania – Serbia – Hungary, May 11-12, 2006. Temesvar, Romania, Abstracts, Temesvar, 2006. p. 53.
6. Tombácz, E.; **Majzik, A.**; Czibulya, Zs.; Kovács, K.: *Particle network formation in soils: is there aggregating or dispersing effect of humic substances?* IAP 2006, IV International Conference on Interfaces Against Pollution, June 4-7, 2006. Granada, Spain, Book of Abstracts, p.36-37.
7. **A. Majzik**, E. Tombácz: *Dispersing and aggregating effect of humic acids and calcium ions in mixed suspensions of montmorillonite and hematite*, poster, 20<sup>th</sup> ECIS and 18<sup>th</sup> ECIC, Sept. 17-22, 2006. Budapest, Hungary, Book of Abstracts, p.419.
8. **A. Majzik**, E. Tombácz: *Dispersing/aggregating effect of humic acids and calcium ions in mixed suspensions of montmorillonite and hematite*, 13<sup>th</sup> Symposium on Analytical and Environmental Problems, September 25, 2006. Szeged, Hungary
9. E. Tombácz, D. Bica, A. Hajdú, E. Illés, **A. Majzik**, L. Vékás: *Surfactant double layer stabilized magnetic nanofluids for biomedical application*, 11<sup>th</sup> International Conference on Magnetic Fluids ICMF 11, July 23-27, 2007. Košice, Slovakia

10. **A. Majzik**, E. Tombácz: *Elastic network of lamellar particles formation and rheological characterization*, Rheofuture Conference, July 1-2, 2004. Karlsruhe, Germany,  
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11. **A. Majzik**, E. Tombácz: *Kölcsönhatások montmorillonit, magnetit, huminsav és kalcium-ion tartalmú összetett vizes diszperziókban*, XXVIII. Kémiai Előadói napok, Október 24-25, 2005. Szeged, Program és előadás-összefoglalók, p. 87.

### Other publications

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14. **Majzik A.**, Tombácz E.: *Szintetikus rétegszilikát hordozóra vitt ZnO/Zn(OH)<sub>2</sub> kompozitok*, XXVII. Kémiai Előadói napok, Október 24-25, 2004. Szeged, Program és előadás-összefoglalók, p. 147.
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### Lectures related to the Ph.D. theses

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