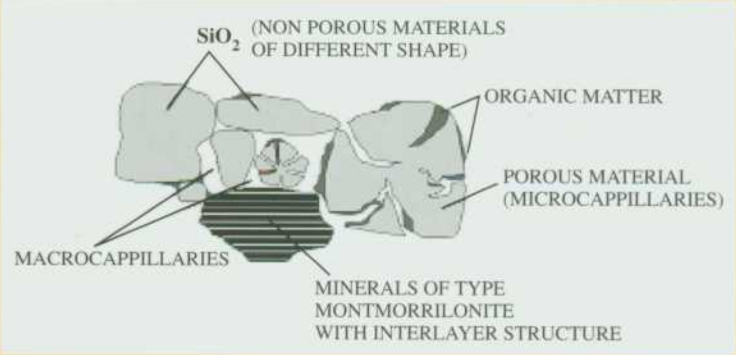
PHYSICOCHEMICAL CHARACTER OF SOIL ADSORBENT

EDITED BY
TOSHO RAYTCHEV, GRZEGORZ JÓZEFACIUK
ZOFIA SOKOŁOWSKA, MIECZYSŁAW HAJNOS



Centre of Excellence for Applied Physics in Sustainable Agriculture AGROPHYSICS

Nikola Poushkarov Institute of Soil Science

Institute of Agrophysics Polish Academy of Sciences

EU 5th Framework Program QLAM-2001-00428

EU 5th Framework Program
QLAM-2001-00428

PHYSICOCHEMICAL CHARACTER OF SOIL ADSORBENT

MULTI AUTHORS WORK

EDITORS:
Tosho Raytchev
Grzegorz Józefaciuk
Zofia Sokołowska
Mieczysław Hajnos

Lublin – Sofia 2005

ISBN 83-87385-98-0

1st Edition: 180 copies

Project of cover: Grzegorz Józefaciuk
Computer edition and technical assistance:
Dorota Matyka-Sarzyńska and Krzysztof Józefaciuk

Print: Drukarnia *ALF-GRAF*, ul. Kościuszki 4, 20-006 Lublin

PREFACE

Soil is the most important part of our living space and our primary duty is to keep its proper functioning to provide harmonized use of the environment and its protection against degradation. Therefore much attention has been paid to better understand of soil properties and processes.

Soil is a polydispersive, multicomponential, multifacial and non-equilibrium system wherein vast number of processes occur in interfacial zone between solid phase and liquid and gaseous phases. The largest amount of this interface belongs to finest soil particle fraction composed from clay minerals, silica, sesquioxides, humus and many others. This fraction is also called soil sorption complex or soil adsorbent.

Knowledge on the properties of soil adsorbent are necessary for description and modeling of many soil features and processes as fertility, mass and energy exchange, accumulation of various species, water retention, microbial life, catalysis, pollution, acidification and alkalization, soil organic matter leaching and oxidation.

Physical chemistry provides specific tools that are helpful in understanding soil adsorbent properties and behavior. Therefore in a frame of a cooperation between Polish and Bulgarian Academies of Sciences involving Institute of Agrophysics PAS in Lublin and Nikola Poushkarov Institute of Soil Science in Sofia, some scientists have been dealing with the above problems for a long time. This cooperation has been strengthen and enlarged as a result of the activity of a Polish-Bulgarian workgroup organized in a frame of the activity of the Centre of Excellence for Applied Physics in Sustainable Agriculture AGROPHYSICS and with financial support of European Commission and Polish State Committee for Scientific Research.

This issue shows some results obtained by this workgroup in a field of soil physical chemistry with special attention placed on surface properties soil adsorbent.

THE EDITORS

CONTENTS:

STRUCTURAL-ADSORPTION STATE OF THE SOIL ADSORBENT AT MACRO-AGGREGATIVE LEVEL OF THE SOIL ORGANIZATION

Raytchev T.[1], Rousseva S.[1], Mehandjiev D.[2]
Jozefaciuk G.[3], Sokolowska Z.[3]

[1] N. Poushkarov Institute of Soil Science, 7 Shosse Bankja Str., 1080 P.O. Box 1369, Sofia, Bulgaria
[2] Institute of General and Inorganic Chemistry, Bulgarian Academy of Science, Sofia, Bulgaria
[3] Institute of Agrophysics, Polish Academy of Sciences, Doswiadczalna 4, P.O. Box 201, 20-209 Lublin, Poland

Abstract

Based on soil samples from three horizons of each Eutric Planosol and Eutric Vertisol, structural-adsorption state has been studied as well as reflection of the inherent colloidal complex on the studied characteristics. Simultaneously, an attempt has been made to investigate the efficiency of the treatments applied (electro-dialysis and treatment by H_2O_2) on the changes of the studied indicators.

The basic hypothesis of the investigation is the assumption for linkage between the porosity of the colloid aggregates and their individual properties, which affects also the structural organization of the soils at macro-aggregative level.

The established changes in the studied structural-adsorption characteristics show that the impact of electro-dialysis is stronger than the treatment by hydrogen peroxide. The efficiency of the applied treatments depends on:

- The amount and the dominating type of clay minerals in the soil;
- Content of humic substances;
- The manner of bond in the organic-mineral associations.

Analysis of the obtained results gives an idea of the relation between the established parameters and the amount of the soil colloids. Simultaneously, information is obtained about the dominating type of the clay minerals involved in the construction of the porous structure corresponding to the data for the mineral composition of the studied soils. It should be noted that the basic bearers of the soil porosity and its surface – the soil clays and humic substances exist at highly diluted condition in the entire soil volume. It can be expected that more detailed information on their contribution and role in the creation of the structure of the soil adsorbent would be obtained whilst investigating its individual characteristics after its extraction from the soil.

INTRODUCTION

In conformity with the genesis of its formation, the soil adsorbent behaves as a colloidal macro-anion, which heterogeneous structure enables the origin of adsorption centres of diverse strength with acid. Its unlimited matrix is a natural composite of soil clays, which surface is naturally modified by the soil organic matter and the inorganic exchangeable cat ions. It is formed in the course of the humus development from the dissociation products of the fermentative destruction of condensed organic compounds and partial bond of their active components with the mineral colloids (Orlov, 1985). The nature of the colloid organization and development of porous structure of the soil adsorbent is a consequence of combination of the insoluble highly-dispersive mineral particle with organic residua of humic character at presence of free hydroxides, mostly silicon, aluminium and iron.

Sorption potential determining ions of the primary organic-mineral kernel (hydroxide, phosphate, silicon, carboxyl, etc.) are located on the surface of their colloid associations while compensating anions (exchangeable cat ions) are distributed partly in the immobile and in the entire mobile diffusion layer. Their activity is functionally related to the porosity of the colloidal aggregates as it is determined by the individual properties of the adsorbent and the availability of its surface for the respective processes. Knowledge on its structural-adsorption status is essential to surmount successfully the multitude problems related to the kinetics and the dynamics of the sorption processes as well as to its sensitivity towards natural or anthropogenic soil degradation processes.

This paper presents the results obtained from a study on the structural-adsorption state of the soil adsorbent and the involvement of its basic components in its porous structure development. The study has been carried out in two stages, the first of which investigates the influence of the soil colloids on the macro-aggregative level of soil organization and the second one – the individual characteristics of the soil adsorbent after its extraction from the soil.

MATERIALS AND METHODS

1. Soils

The study is accomplished with soil samples from three horizons of Eutric Planosol (Velchevo village, Lovech district) – A_1 (0 – 15 cm); B_2 (62 – 82 cm); C_1 (112 – 140 cm) and Eutric Vertisol (Sredetz village, Stara Zagora district) – A_{plowgh} (0 – 25 cm); B_1 (62 – 90 cm); C_1 (120 - 130 cm). Both soils are in the transitory-continental sub-zone (Subev, 1960).

The Eutric Planosol has well developed differentiation with respect to the profile distribution of the clay fraction (Tab.1). Its reaction changes from strongly acid (horizon A_1) to slightly alkaline (horizon B_2). The clay minerals in the surface horizon are represented mostly by aluminiferous chlorite (21%), hydro-mica (16%) and kaolinite (16%). Significant amounts of no-silicon compounds of Si, Al и Fe (6%) are found as well as notable presence of fine-dispersive quartz (31%) (Atanassov, 1977; Atanassov and Dimitrov, 1976). The montmorillonite (37%) dominates in the composition of the clay minerals in the illuvial horizon, followed my the hydro-mica (19%) and the kaolinite (14%), while the amount of fine-dispersive quartz (13%) decreases markedly compared to the top horizon an the no-silicon compounds of Si, Al и Fe show a slight trend to increase (7%) (Atanassov, 1977). The distribution of the clay minerals in the horizon C is similar but the montmorillonite content is the highest (44%).

The Eutric Vertisol has a clayey texture without noticeable differences of the contents of clay and silt fractions in the particular genetic horizons. The clay is the dominant fraction in this soil. There is no significant heterogeneity in the amount of the clay minerals down the soil profile. In their composition dominate these of the montmorillonitic group (~ 70%), followed by illite (~ 14%) and kaolinite (~ 10%). There are also certain amounts of hydro-goethite (~ 5.0%) (Atanassov, 1977). The value of pH varies from 7.3 to 8.0.

2. Treatments and methods for investigation

The initial soil samples have been a subject to the following treatments:

- Treatment by hydrogen peroxide accompanied by heating on a water bath (Jackson, 1958);
- Electro-dialysis (Raytchev, 1996; Raytchev, 1997; Raytchev and Toncheva, 1997);

The electro-dialysis is accomplished in three-chamber apparatus with a capacity of 0.250 l of each chamber at constant values of the voltage (250 V), field gradient (50 V/cm) and using cellophane membranes (Bolshakov, 1978; Kozhuharov and Alyoshin, 1962). The treatment has been executed carefully on account of the clay minerals susceptibility to easy disintegration at higher current density (Ovcharenko, 1960; Tarasevich and Ovcharenko, 1975). The control has been fulfilled by periodical measurement of the suspension pH in the middle chamber and the extract in both outlying chambers (Raytchev, 1996).

The specific surface area (S_{BET}) of the initial samples and these treated by the methods noticed above has been determined by the method of BET using data from low-temperature adsorption of nitrogen vapours (Brunauer et al., 1938). The calculations are completed by the formula:

$$S_{BET} = (V_m/22415) \times N_A \times \omega \times 10^{-20} \ m^2/g$$

where:

V_m – capacity of the mono-layer, cm^3/g;

ω – area occupied by an adsorbat's molecule in the filled-in mono-layer (the molecule cross-sectional area), Å^2. $\omega_N = 16.2$Å^2 (0.162 nm^2) for N_2 (Gregg and Sing, 1967);
$N_A = 6.023 \times 10^{23}$ mol^{-1} – Avogadro number, molecules per mol;
22415 cm^3 mol^{-1} – molar volume.

The capacity (V_m) and the adsorption heat (c) of the mono-layer have been determined graphically from the isotherms using the linear form of the BET equation:

$$x / [V(1 - x)] = 1 / (V_m .c) + [(c - 1) / (V_m . c)] .x, \qquad (1)$$

where:
$x = P/P_o$;
P – pressure of the saturated vapours above the adsorptive at certain temperature T;
P_o – external pressure;
P/P_o – relative vapour pressure;
V – volume of the absorbed gas at relative pressure of P/P_o;
c – adsorption heat of the mono-layer.

The pore-size distribution has been studied following both branches of the complete isotherms (Orr and Dalla Walle, 1959; Innes, 1957; Gregg and Sing, 1967; Anedrson, 1972):

$$\frac{\Delta V}{\Delta r} \cdot \frac{1}{V_0} \cdot 10^2 \qquad (2)$$

where:
ΔV – volume of the filled pores corresponding to Δr;
V_0 – total pore volume.

The surface area of the transitional pores (S_p) and the volumes of micro- (V_μ) and transitional (V_p) pores have been calculated on the basis of adsorption data (Kiselev, 1958; Dubinin, 1965; Dubinin, 1970):

$$S_p = \frac{1}{\gamma} \int_{\alpha_i}^{\alpha_{\max}} A_0 \times d\alpha \ , \qquad (3)$$

where:
$A_0 = RT \ln P/P_0$ – differential work for adsorption of the nitrogen vapours;
α_i – adsorption value at the beginning of the hysteresis, mmol/g;
α_{max} – maximal adsorption amount at $P/P_0 = 1.0$;
γ – surface tension of the liquid adsorbate.

It should be noted that this equation is well applicable for calculating the specific surface of macro- and transitionally-porous adsorbents but results in reduced assessment for micro-porous adsorbents, which pores are filled volumetrically in the mere adsorption region – before the beginning of the capillary condensation. At adsorbents with strongly developed transitional porosity, the liquid volume adsorbed in the beginning of the hysteresis is a sum of two volumes. The one of them corresponds to the volume of micro-pores, and the other – to the volume of the adsorbed layer at the surface of the transitional pores (Komarov, 1977). However, determination of the volume of micro-pores is worthwhile only for an adsorbent with $\alpha_i - \alpha_m > 0$, where α_m is the capacity of the mono-layer in mmol/g, calculated by the BET method. Adhering to this inequality, the volume of micro-pores is calculated by the formula:

$$V_\mu = (\alpha i - a.S_p).v, \qquad (4)$$

where:
a – adsorption magnitude per unit free surface ($a_N = 0.0102$ mmol/m^2 for N_2);
v – volume of 1mmol adsorbate in a form of liquid ($v_N = 0.0346$ cm^3/mmol for N_2).

The volume of transitional pores (V_p) has been determined as a difference between the total volume of the sorption space ($V_0 = \alpha_{max}.\ v$) and the volume of micro-pores (V_μ): $V_p = V_0 - V_\mu$.

The interpretation of the obtained data is based on the Dubinin's classification (Dubinin, 1970; 1972), which distinguishes between micro-pores (< 2 nm), transitional or meso-pores (2÷200 nm) and macro-pores (>200 nm) according to the effective pore radius.

RESULTS

Capillary condensational hysteresis of near type is observed on the isotherms of all initial samples (Figs. 1 - 5), regardless of the type of treatment. An exception to this observation show the isotherms of the samples form A_1 horizon of Eutric Planosol, which are of the first type according to the BDDT classification (Brunauer et al., 1940). This exception is most likely to be a result of the presence of high amount of non-porous adsorbents, which is confirmed by the particle-size distribution of this sample (Atanassov and Dimitrov, 1976). The clay fraction is 14% and there is a great amount of kaolinite and fin-dispersive quartz. The hysteresis appearance at the other studied soil samples is an indication for the increased amount of porous adsorbent, which enable capillary condensation. These are mostly clay minerals of 2:1 type composing the clay fraction, which content is > 40% (Tab. 1). The specific surface area (S_{BET}) of the initial samples is in the ranges 21 ÷ 55 m^2/g – for the Eutric Planosol and 76 ÷ 82 m^2/g – for the Eutric Vertisol (Tab. 1).

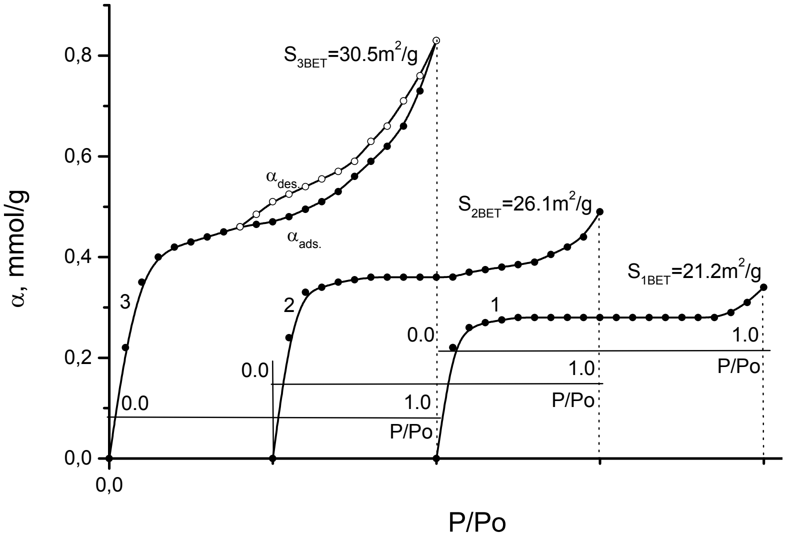


Fig. 1. Low-temperature nitrogen adsorption-desorption isotherms for soil from layer A of Eutric Planosol (each isotherm is shifted along the abscissa by P/Po = 0.5). α – adsorbed amount, mmol/g; 1 – untreated; 2 – treated with H_2O_2; 3 – electrodialysed.

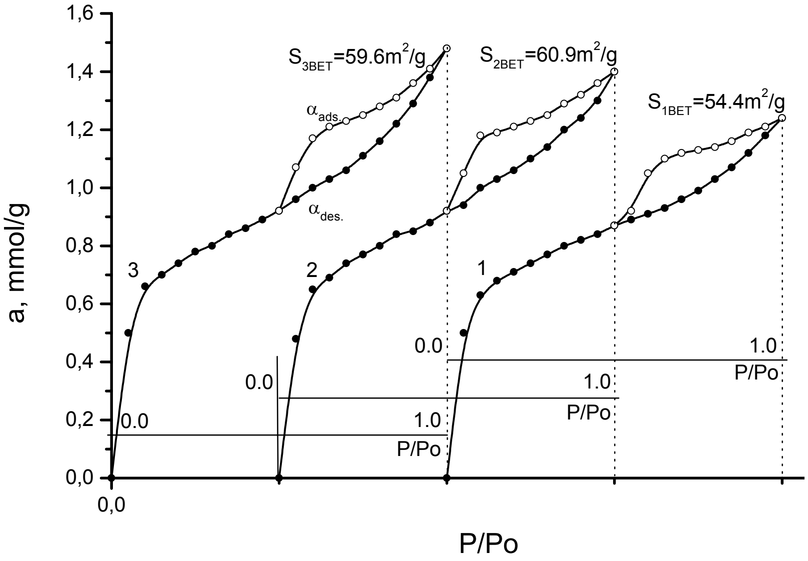


Fig. 2. Low-temperature nitrogen adsorption-desorption isotherms for soil from layer B of Eutric Planosol (each isotherm is shifted along the abscissa by P/Po = 0.5). α – adsorbed amount, mmol/g; 1 – untreated; 2 – treated with H_2O_2; 3 – electrodialysed.

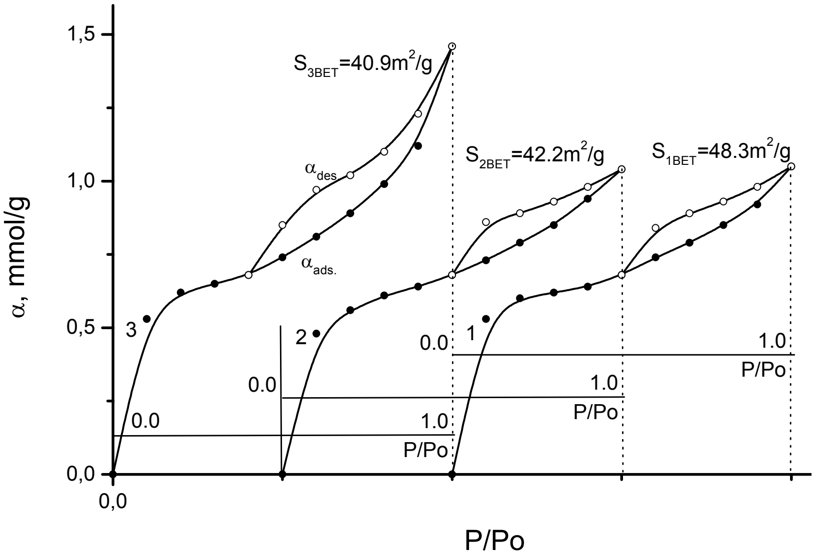


Fig. 3. *Low-temperature nitrogen adsorption-desorption isotherms for soil from layer C of Eutric Planosol (each isotherm is shifted along the abscissa by P/Po = 0.5). α – adsorbed amount, mmol/g; 1 – untreated; 2 – treated with H_2O_2; 3 – electrodialysed.*

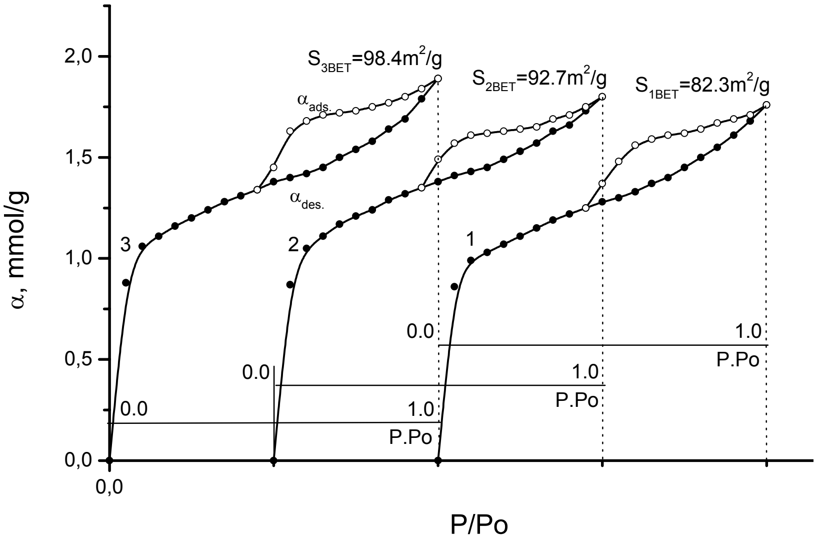


Fig. 4. *Low-temperature nitrogen adsorption-desorption isotherms for soil from layer A of Eutric Vertisol (each isotherm is shifted along the abscissa by P/Po = 0.5). α – adsorbed amount, mmol/g; 1 – untreated; 2 – treated with H_2O_2; 3 – electrodialysed.*

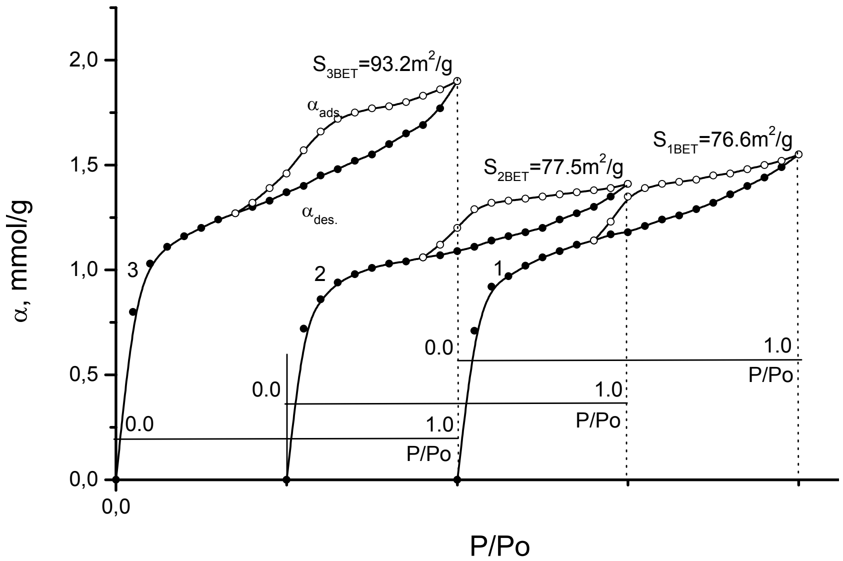


Fig. 5. *Low-temperature nitrogen adsorption-desorption isotherms for soil from layer B of Eutric Vertisol (each isotherm is shifted along the abscissa by P/Po = 0.5).*
α – adsorbed amount, mmol/g; 1 – untreated; 2 – treated with H_2O_2; 3 – electrodialysed.

Table 1. General characteristics of the initial soil samples from Eutric Planosol and Eutric Vertisol

Soil	Horizon depth, cm	pH_{H2O}	Organic C, %	Carbonates, %	Particles < 2 µm, %	Particles < 10 µm, %
Eutric Planosol	A_1 0 - 15	4.5	1.38	-	14.1	44.5
	B_2 62 - 82	5.7	0.93	-	54.0	61.9
	C_1 112 - 140	7.6	0.32	3.2	41.0	56.3
Eutric Vertisol	$A_{орн}$0 - 25	7.3	1.95	-	50.4	66.0
	B_1 62 - 90	7.9	1.22	0.1	52.4	73.5
	C_1 120 - 130	8.0	0.70	19.8	45.2	63.4

The values of the specific surface area for the Eutric Vertisol are similar for the whole soil profile, but S_{BET} for the Eutric Luvisol has its lowest value in the top horizon and increases significantly in the B_2 horizon, remaining the same in the C_1 horizon. This is in conformity with the strong soil textural differentiation down the profile of the Eutric Planosol (Atanassov and Dimitrov, 1976) and its absence in the profile of the Eutric Vertisol (Behar et al.,1969), as well as with the differences between the two soils in the dominant type of clay minerals.

After removal of the soil organic matter by hydrogen peroxide S_{BET} increases for the samples from the top horizons of both soils as well as for the sample from B_2 horizon of the Eutric Planosol (Tab. 2).

Table 2. Structural-adsorption characteristics of soil samples of Eutric Planosol (EP) and Haplic Vertisol (HV). 1 – initial sample; 2 – after treatment with H_2O_2; 3 – after electro-dialysis; S_{BET} – specific surface area (Brunauer et al., 1938); S_p – surface of the meso-pores (Kiselev, 1958); r – average pore radius (Orr and Dalla Walle, 1959); d – distance between the flat-parallel layers (Innes, 1957); V_μ- volume of micro-pores; V_o – maximal pore volume; V_p- volume of meso-pores.

Soil / Horizon		Sample No.	S_{BET}, m^2/g	S_p, m^2/g	r_p, Å	d, Å	Pore volume, recalculated with respect to the liquid volume, $(cm^3/g)x10^2$			Organic carbon, %
							V_o	V_p	V_μ	
EP	A_1	1	21.2							1.38
		2	26.1							0.55
		3	30.5	12.3			2.8	1.6	1.2	1.64
	B_2	1	54.4	15.3	14.8	30	4.3	1.9	2.4	0.93
		2	60.9	15.8	14.8	30	4.8	2.3	2.5	0.51
		3	59.6	21.1	18.6	30	5.1	2.7	2.4	0.98
	C_1	1	48.3	13.2	18.6	30	3.6	1.6	2.0	0.32
		2	42.2	17.3	18.6	30	3.6	1.9	1.7	0.22
		3	40.9	26.1	14.8	25	5.1	3.4	1.7	0.40
HV	$A_{орн}$	1	82.3	21.3	14.8	30	6.1	2.4	3.7	1.95
		2	92.7	20.2	14.8	25	6.8	2.0	4.8	0.50
		3	98.4	22.8	14.8	30	7.5	3.7	3.8	2.17
	B_1	1	76.6	21.7	14.8	25	5.4	2.2	3.2	1.22
		2	77.5	18.4	18.6	25	4.9	1.9	3.0	0.59
		3	93.2	35.1	18.6	30	6.5	3.3	3.2	1.58
	C_1	1	78.8	9.6	14.8	30	4.6	1.1	3.5	0.70

There is no similar effect for the rest of the soil samples or it is slightly expressed. The total pore volume (V_0) does not change but there is a tendency to slight redistribution between the volumes of micro- (V_μ) and meso-pores(V_p), which affects also the surface areas of the latest (S_p) (Figs. 6-7).

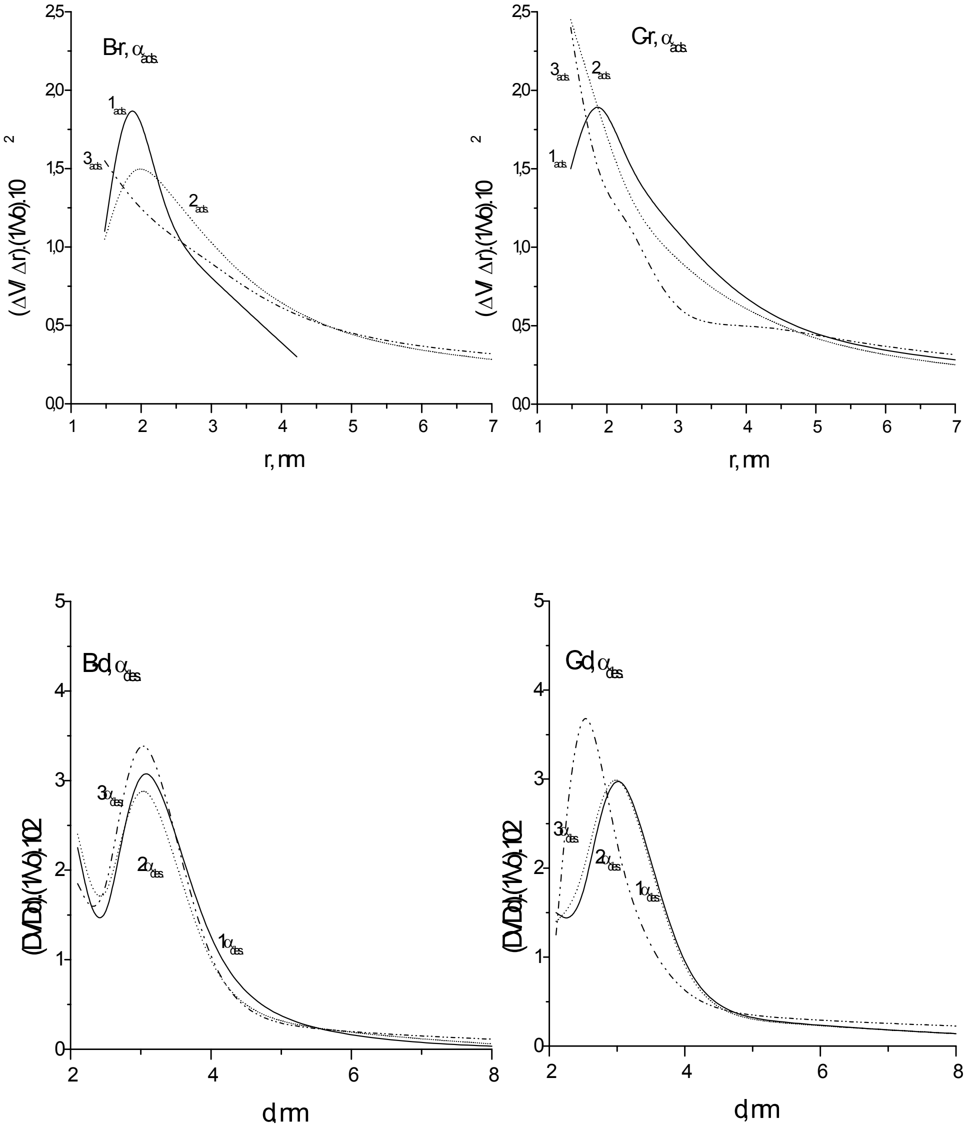


Fig. 6. *Pore-size distribution for layer B (B) and layer C (C) of Eutric Planosol calculated by the method of Orr and Dalla Walle (r, $\alpha_{ads.}$); by the method of Innes (d, $\alpha_{des.}$).*
1 – untreated; 2 – treated with H_2O_2; 3 – electrodialysed; ΔV – volume of the filled pores corresponding to Δr; Vo – total pore volume.

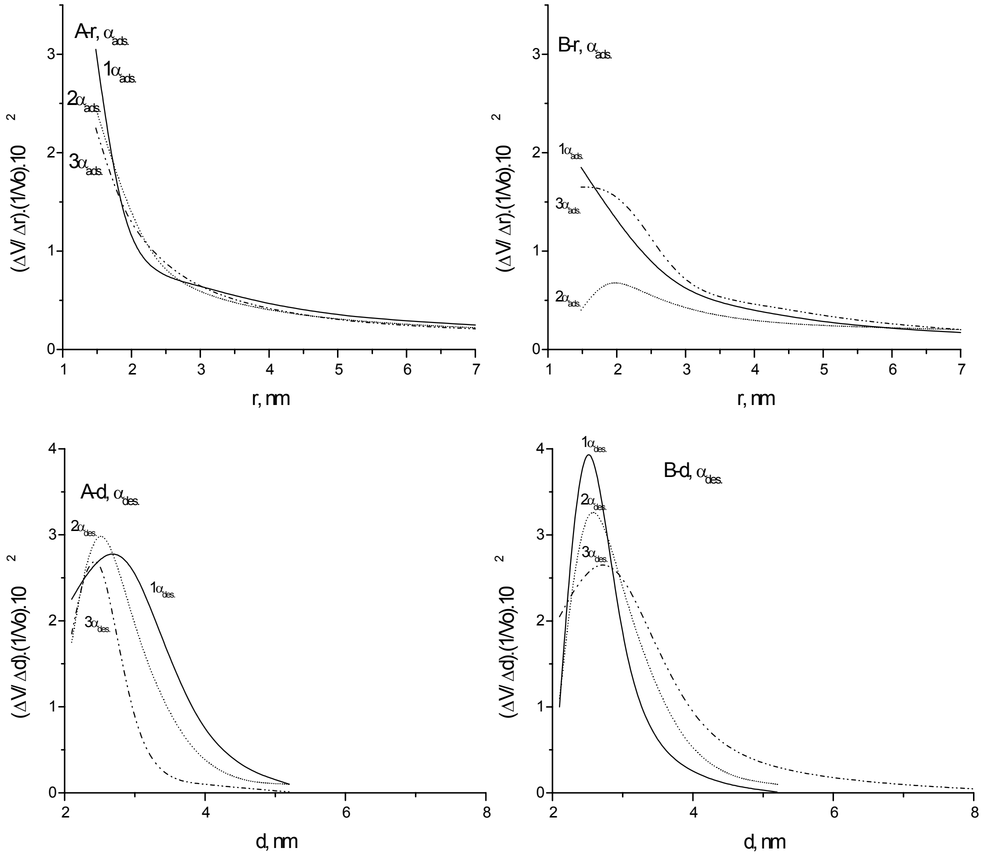


Fig. 7. *Pore-size distribution for layer A (A) and layer B (B) of Eutric Vertisol calculated by the method of Orr and Dalla Walle (r,* $\alpha_{ads.}$*); by the method of Innes (d,* $\alpha_{des.}$*).*
1 – untreated; 2 – treated with H_2O_2*; 3 – electrodialysed; ΔV – volume of the filled pores corresponding to Δr; Vo – total pore volume.*

The same conclusions refer to the structural-adsorption characteristics of the soil samples submitted to electro-dialysis (Tab. 2). It should be noted that hysteresis appears on the isotherm of the sample from A_1 horizon of the Eutric Planosol after this treatment (Fig. 1). It is most likely that this is a result from the dispersion of the particles during the process and disintegration of the eventually presenting valence bonds between the clay minerals and the humus substances at low values of pH. Besides, it is possible an opening of additional pore volume at the lateral surfaces of these minerals where capillary condensation can take place. The strong increase of the surface area of meso-pores (S_p) after this treatment (Tab.2) proves similar opportunity.

The changes established for the studied structural-adsorption characteristics show that the impact of the electro-dialysis is stronger than the treatment by hydrogen peroxide. The efficiency of the applied treatments depends on:

- The amount and the dominant type of clay mineral in the soil;
- Content of humus substances;
- The manner of bond in the organic-mineral associations.

The admissibility of such statement is based on the following observed facts:

A. The efficiency of both treatments is the highest when clay minerals of kaolinic type dominate and the humus content is high (A_1 horizon – Eutric Planosol). The strongest impact of the electro-dialysis in this case, compared to the rest of the studied samples, can be related to the possibility for breaking also some valence bonds between the octahedral surfaces of these clay minerals and the humus substances. Their formation in the conditions of strongly acid reaction of this soil in the A horizon is very likely.

B. The efficiency of both treatments decreases when the clay minerals of montmorillonitic type dominate and there is still significant presence of kaolinic minerals, but reduced content of humus substances (B_1 horizon – Eutric Planosol).

C. The efficiency of both increases at significant content montmorillonitic minerals and high humus content (A_{plough} – Eutric Vertisol). Regardless of the absence of valence bonds in the organic-mineral association, S_{BET} after electro-dialysis in this case (A_{plough} and B_2 – Eutric Vertisol) increases strongly, which can be explained by disaggregation of the particles and release of new surfaces with large area, inherent to the mineral type 2:1. The effect of the treatment by hydrogen peroxide is negligible at the same content of montmorillonitic minerals but reduced humus content (B_2 horizon – Eutric Vertisol).

CONCLUSIONS

The most general analysis of the obtained results gives an idea about the relation between the established parameters of the studied indicators and the amount of the soil colloids. At the same time, information is obtained for the dominant type of clay minerals involved in the formation of the porous structure, which corresponds to the data for the mineral composition of the studied soils. It should be noticed that the basic bearers of soil porosity and its surface – the soil clays and humus substances are at severely diluted condition in the entire soil volume. It can be expected that more detailed information on their involvement and role in formation of the structure of the soil adsorbent and its adsorption surfaces can be obtained at studying its individual characteristics after its extraction from the soil.

REFERENCES

Anderson, R., 1972. Experimental methods for studying the catalysis. Publ. “Mir”, M, p.480. (Ru)

Atanassov, Iv., 1977. Weathering and evolution of mineral part of the soils in Bulgaria. D. Sci. Thesis, Higher Agric. Inst., Sofia, p.566. (Bg)

Atanassov, Iv., D. N. Dimitrov, 1976. Distribution of the fine-dispersive minerals within the profile of light-grey gleyic soils. Soil Science and Agrochemistry, (XI) 3:17-25. (Bg)

Behar, A., K. Paskaleva, G. Hubenow, 1969. Clay minerals in the main soils types in Bulgaria. Soil Science and Agrochemistry, 5:21-35. (Bg)

Bolshakov, V., 1978. Application of the method of electro-dialysis for soil studies. Proc. Soil Sci. Inst. Dokuchaev W.W., M. (Ru)

Brunauer, S., L. S. Deming, W. S. Deming, E. J. Teller, 1940. Theory of Van der Waals adsorption of gases. J. Am. Chem. Soc., 62 (7):1723:1732.

Brunauer, S., P. H. Emmet, E. Teller, 1938. Adsorption of gases in multimolecular layers. Journal of American Chemical Society, 60, 309 – 314.

Dubinin, M. M., 1965. Modern State of The Theory of Gas and Vapour Adsorption By Microporous Adsorbents. Pure and Appl. Chem., 10: 309-321.

Dubinin, M. M., 1970. Fundamental problems of the physical adsorption theory. Proc. I All-Union Conf. Theoretical Probl. Adsorption. Publ. “Nauka ”, M., p.476. (Ru)

Dubinin, M. M., 1972. Adsorption and porosity. Proc. All-Union Conf. Theoretical Probl. Adsorption. Publ. “Nauka ”, M., p.360. (Ru)

Gregg, S. J., K. S. W. Sing, 1967. Adsorption, Surface Area and Porosity. Academic Press, London and New York, p.304.

Innes, W. B., 1957. Use of Parallel Plate Model in Calculation of Pore Size Distribution. Anal. Chem., 29: 1069-1073.

Jackson, M. L., 1958. Soil Chemical analysis, New York:Prentice-Hall, p.498.

Kiselev, A. V., 1958. The Structure and Properties of Porous Materials. Ed. D. H. Everett, F. Stone, London, p 195.

Komarov, V. S, 1977. Adsorbents and their properties, Publ. “Nauka I Tehnika ”Minsk. 248 p. (Ru)

Kozhuharov, M., S. N. Alyoshin, 1962. On the progress of separation of exchangeable bases and anions from some Bulgaria soils using electro-dialysis. Higher Agric. Inst. G. Dimitrov, Proc. Agronomy Faculty*, v.* 11, 105-122. (Bg)

Orlov, D. S., 1985. Soil Chemistry. Publ. Moscow University, p.376. (Ru)

Orr, C., J. M. Dalla Walle, 1959. Fine particle measurement, Macmillan, London, p.846.

Ovcharenko, F. D., 1960. Hydrophylicity of Clays and Clay Minerals. Publ. AS USSR, Kiev: p. 292. (Ru)

Raytchev, T., 1997. Kinetics of the desorption of cations. II. Desorption of exchangeable calcium depending on humus quality in the soil, Soil science, Agrochemistry and Ecology, Sofia, vol. XXXII, 4:37-39. (Bg).

Raytchev, T., R. Toncheva, 1997. Kinetics of the desorption of cations. I. A mathematical model testing, Soil science, Agrochemistry and Ecology, Sofia, vol. XXXII, 4:34-36. (Bg).

Raytchev, T., 1996. Influence of organo-mineral interactions on colloid-chemical state of the soil adsorbent. D. Sci. Thesis, “N. Poushkarov” Inst., Sofia, 161 pp. (Bg).

Subev, L., 1960. Agro-climatic manual for Bulgaria, Sofia. (Bg)

Tarasevich, Yu. I., F. D. Ovcharenko, 1975. Adsorption of Clay Minerals. Publ. “Naukova dumka”, Kiev: p.352. (Ru)

Yets, D., 1964. In: “Catalysis. New physical methods and studies ”, Publ. “Mir”, M.: p.372. (Ru)

STRUCTURAL-ADSORPTION STATE OF THE SOIL CLAY FRACTION

Raytchev T.[1], Mehandjiev D.[2], Rousseva S.[1],
Jozefaciuk G.[3], Hajnos M.[3]

[1] N. Poushkarov Institute of Soil Science, 7 Shosse Bankja Str., 1080 P.O. Box 1369, Sofia, Bulgaria
[2] Institute of General and Inorganic Chemistry, Bulgarian Academy of Science, Sofia, Bulgaria
[3] Institute of Agrophysics, Polish Academy of Sciences, 4 Doswiadczalna Str., P.O. Box 201, 20-209 Lublin, Poland

Abstract

The paper presents results from a study on the structural-adsorption state of the soil adsorbent after its extraction from samples of Eutric Planosol and Eutric Vertisol. The studies are carried out with clay fractions and their preparations obtained after treatment with H_2O_2, electro-dialysis, with $H_2O_2 + Na_4P_2O_7$ and electro-dialysis of samples treated in advance with $H_2O_2 + Na_4P_2O_7$.

The observed changes in the structural-adsorption characteristics of the clay fractions confirm the established relationship between the impact of the applied treatments and the amount, and the dominant type of clay minerals in the sample, the humus content and the manner of their bonding in organic-mineral associations. Presented results show that the soil adsorbent of the studied soils can be referred to the sorbents with pronounced meso-porous character, which porous structure is formed by relatively larger flat-parallel pores and micro-voids between or in the walls of the lamellar pores.

Three fractions of the humic substances have been distinguished, discriminated in accordance with their stability, which sensibility towards the applied treatments depends on the strength of the bonds in the organic-mineral associations:

- HS_{clay} – humic substances, most likely involved in the primary organic-mineral matrix ($PM_{HS\text{-}clay}$), which are not affected by the applied treatments;
- $HS_{int.}$ – humic substances, enriched with cyclic-kernel complexes included in the composition of the inner layer ($L_{int.}$), directly bonded with the organic-mineral kernel ($PM_{HS\text{-}clay}$). Probably, this increases its stability towards treatment with H_2O_2, while the electro-dialysis and the treatment with $H_2O_2 + Na_4P_2O_7$ are aggressive sufficiently for breaking its specific bond with $PM_{HS\text{-}clay}$;

- $HS_{back.}$ – humic substances of fulvic type bonded by cation bridge bond with the internal layer ($L_{int.}$), which form the external layer ($L_{back.}$) of the soil adsorbent (SA). Availability of a large number of functional groups in their long-chain molecules and the presence of polyvalent cations enable bonding of individual organic-mineral units into more compact aggregates by bridge mechanism of flocculation. It should be assumed that this bond is more stable and its strength approaches that of $L_{int.}$ - $PM_{HS\text{-}clay}$, but the treatments applied in this study cannot distinguish between these.

It is indicated that both kinds of bonds are relatively weak and sensible to chemical or microbial attack because of the point character of structure formation and they are unstable at treatment by hydrogen peroxide. The main cause for the absence of a dense contact between the phases is the conformal inhomogeneity of the contacting phases and reduces the strength of the bond between them. Besides the opening of the medium layer of the soil sorbent, its disintegration enables additional disaggregation, which reflects on the total area of the surfaces opened by these two effects.

INTRODUCTION

The study on the structural-adsorption state at micro-aggregative level of soil organization reveals its dependence on the amount and the dominant type pf clay minerals in it, its humus content and the manner of bonding in the organic-mineral associations. However, the character of such study, being rather orientative, cannot submit sufficiently reliable information about the character of the porous structure and the type of the related porous spaces. It is not possible either to distinguish well enough between the involvements of the diversely stable organic components of the soil adsorbent in the formation of its structure.

This part of the paper presents the results from a study on the structural-adsorption state of the soil adsorbent after its extraction from the soil. The studies are accomplished with clay fractions of the selected soils (Eutric Planosol and Eutric Vertisol), while the extraction is carried out without applying chemical treatment.

MATERIALS AND METHODS

1. Soils

The study is performed on clay fractions extracted without preliminary chemical treatment (Aydinyan, 1966) of soil samples from three horizons of Eutric Planosol (Velchevo village, Lovech district – A_1 horizon (0 – 15 cm); B_2 horizon (62 – 82 cm); C_1 horizon (112 – 140 cm) and Eutric Vertisol (Sredetz village, Stara Zagora region – A_{plough} horizon (0 – 25 cm); B_1 horizon (62 – 90 cm); C_1 horizon (120 - 130 cm).

The main soil characteristics, presented in the firs part of the study (structural-adsorption state at macro-aggregative level of the soil organization), show well expressed differentiation with respect to the profile distribution of the clay content at the Eutric Planosol and its absence at the Eutric Vertisol.

The clay minerals in the top horizon of the acid soil are presented mostly by aluminiferous chloride (21%), hydro-mica (16%) and kaolinite (16%), while montmorillonitic minerals dominate in the lower horizons (Atanassov, 1977; Atanassov and Dimitrov, 1976). The content of montmorillonite is highest (44%) in C_1 horizon.

There is no significant quantitative heterogeneity of the clay minerals in the soil profile depts of the Eutric Vertisol. These of the montmorillonitic group dominate (~ 70%) in their composition, followed by illite (~ 14%) and kaolinite (~ 10%). Certain amount of hydrogoethite (~ 5.0%) is established as well (Atanassov, 1977).

2. Treatments and methods of study

Samples from the extracted clay fractions have been treated as follows:

- Treatment with H_2O_2 accompanied by heating on a water bath (Jackson, 1958);
- Treatment withH_2O_2 + 0.1M $Na_4P_2O_7$ at the same conditions;
- Electro-dialysis of the initial samples (Raytchev and Toncheva, 1997);
- Electro-dialysis of samples preliminary treated with H_2O_2 + 0.1M $Na_4P_2O_7$.

The electro-dialysis is completed in three-chamber apparatus with a capacity of 0.250 l of each chamber, at constant voltage (250 V), field gradient (50 V/cm) through cellophane membranes (Bolshakov, 1978; Kozhuharov and Alyoshin, 1962; Raytchev, 1996). The conditions were controlled by periodical measurement of pH of the suspension in the middle chamber and of the extract in the outlying chambers.

The humus content has been determined by modified method of Turin by oxidation with bichromate /H_2SO_4 at 120°C for a period of 45 min and catalyst Ag_2SO_4 and reverse titration with $(NH_4)_2SO_4.FeSO_4.6H_2O$ (Kononova, 1966).

The specific surface area (S_{BET}) of the initial samples and these treated by the noticed methods has been determined by the BET method on the basis of data from low-temperature adsorption of nitrogen vapours (Brunauer et al., 1938).

The capacity (V_m) and the adsorption heat (c) of the mono-layer have been determined graphically from the isotherms drawn to the respective relative vapour pressure (P/P_o) using the linear form of the BET equation (Brunauer et al., 1938).

The pore-size distribution has been studied following both branches of the complete isotherms (Orr and Dalla Walle, 1959; Innes, 1957; Gregg and Sing, 1967; Anderson, 1972):

$$\frac{\Delta V}{\Delta r} \cdot \frac{1}{V_0} \cdot 10^2 \tag{1}$$

where:

ΔV [$m^3 kg^{-1}$] – volume of the filled pores corresponding to Δr [m];

V_0 [$m^3 kg^{-1}$] – total pore volume.

The surface area of the meso-pores (S_p) and the volume of the micro-pores (V_μ) have been calculated on the basis of adsorption data for the adsorption value at the hysteresis beginning (α_i, mmol/g) and the maximum adsorbed amount (α_{max}) при $P/P_0 = 1.0$ (Kiselev, 1949; Dubinin, 1965; Dubinin, 1970). The volume of meso-pores (V_p) has been determined as a difference between the total sorption space (V_0) and the volume of micro-pores: $V_p = V_0 - V_\mu$.

The interpretation of the obtained data is based on the Dubinin's classification (Dubinin, 1970; 1972), which distinguishes between micro-pores (< 2 nm), transitional or meso-pores (2÷200 nm) and macro-pores (>200 nm) according to the effective pore radius.

RESULTS

The low-temperature adsorption isotherms on nitrogen vapours of the samples of clay fractions of both soils have S-shaped mode with well pronounced capillary-condensation hysteresis, which in most cases exists till relative pressure of P/Po = 0.3 ÷ 0.5 (Figs. 1-6). There is a certain shift toward lower values of P/Po in this interval for the samples of the Eutric Planosol (Figs. 1-3).

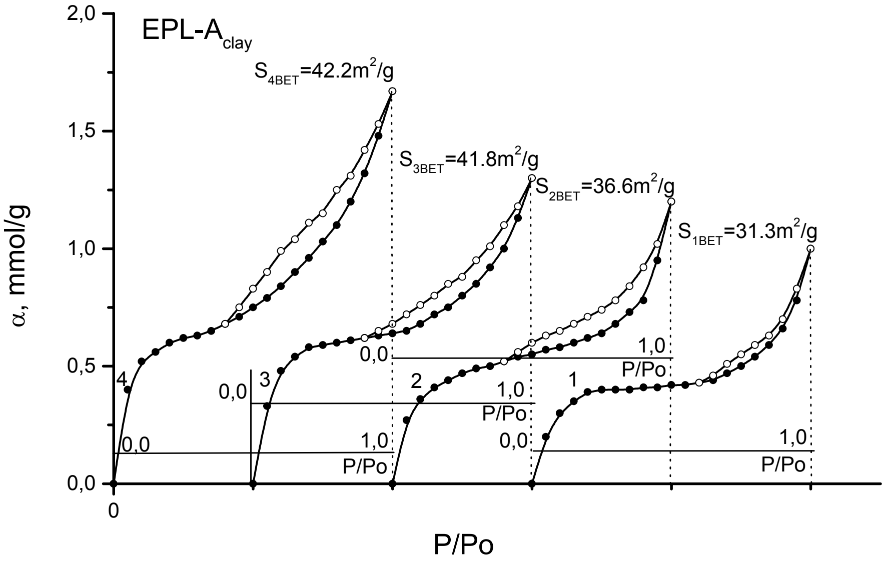


Fig.1. *Low-temperature nitrogen adsorption-desorption isotherms for < 2 μm clay fractions isolated from layer A of Eutric Planosol (EPl-A$_{clay}$)*
Each isotherm is shifted along the abscissa by P/Po = 0.5. α – adsorbed amount; 1 – untreated; 2 – treated with H_2O_2; 3 – electodialysed; 4 - treated with H_2O_2 + $Na_4P_2O_7$.

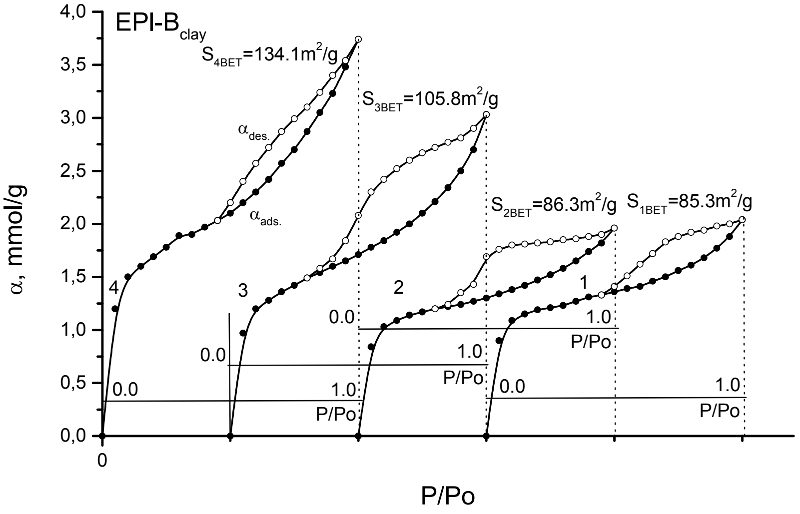


Fig. 2. *Low-temperature nitrogen adsorption-desorption isotherms for < 2 µm clay fractions isolated from layer B of Eutric Planosol (EPl-B_{clay}). Abbreviations as in Fig. 1.*

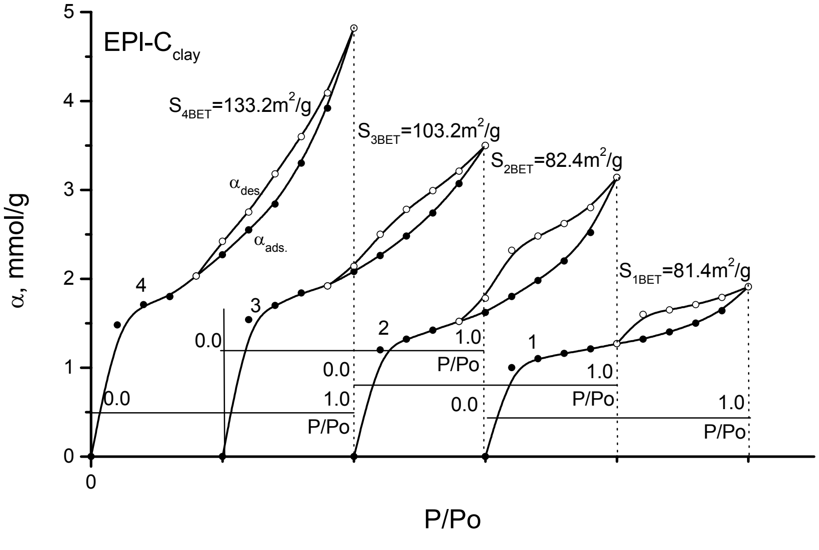


Fig. 3. *Low-temperature nitrogen adsorption-desorption isotherms for < 2 µm clay fractions isolated from layer C of Eutric Planosol (EPl-C_{clay}). Abbreviations as in Fig. 1.*

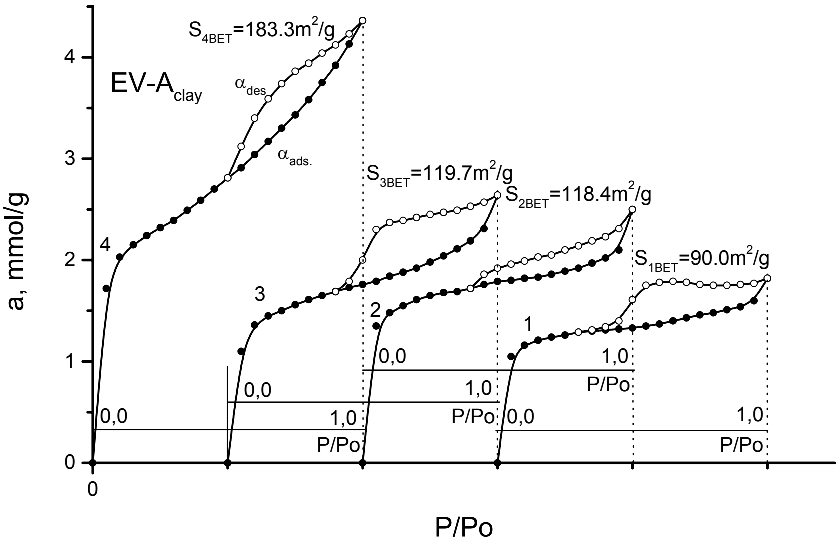


Fig. 4. *Low-temperature nitrogen adsorption-desorption isotherms for < 2 µm clay fractions isolated from layer A of Eutric Vertisol (EV-A$_{clay}$). Abbreviations as in Fig. 1.*

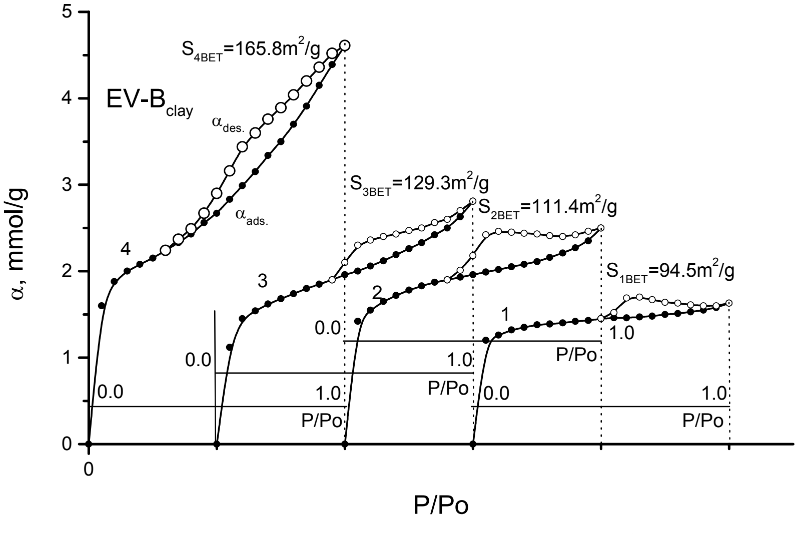


Fig. 5. *Low-temperature nitrogen adsorption-desorption isotherms for < 2 µm clay fractions isolated from layer B of Eutric Vertisol (EV-B$_{clay}$). Abbreviations as in Fig. 1.*

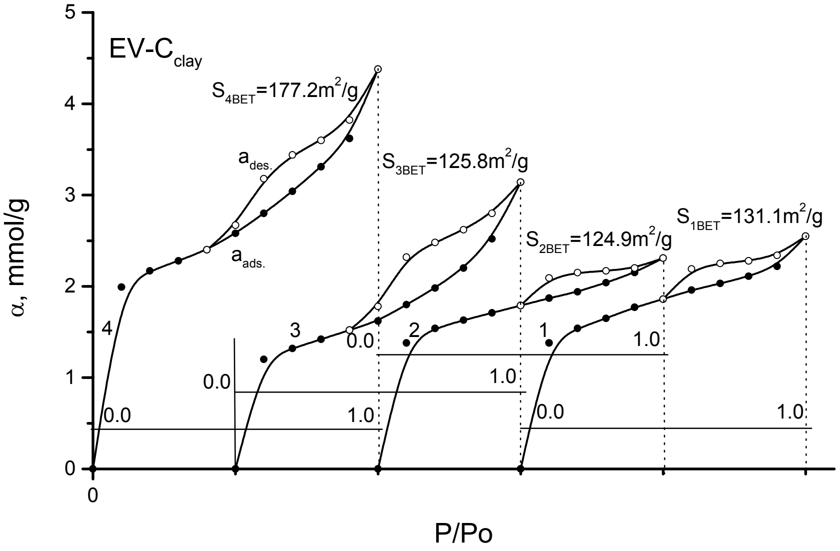


Fig. 6. *Low-temperature nitrogen adsorption-desorption isotherms for < 2 µm clay fractions isolated from layer C of Eutric Vertisol (EV-C$_{clay}$). Abbreviations as in Fig. 1.*

At P/Po → 1.0 sharp increase characterizes almost all the isotherms, which assumes a presence of pores with radius r > 30 nm. The adsorption value at the beginning of the hysteresis is higher than the capacity of the mono-layer, which is conditioned by the presence of a certain amount of micro-pores available for the nitrogen molecules. The clear capillary-condensation character is an indication for the meso-pore nature of the structure of the clay minerals, which are the main element of the soil adsorbent.

This most general analysis of the adsorption-desorption isotherms gives grounds for referring the studied clay fractions to the sorbents with heterogeneous porous structure.

The increased adsorption capability in the entire interval of P/Po of the clay fractions from the Eutric Vertisol (Figs. 4-6), compared to the Eutric Planosol, can be explained with the increased dispersibility of the Vertisol and consequently – higher value of and larger volume of the adsorption space. This is in accordance with the increased content of montmorillonitic minerals in this soil, at which the internal surface area dominates over the external one. There is higher content of kaolinite, hydro-mica and fine-dispersive quartz in the Eutric Planosol, which are with low surface area and undeveloped porosity.

S_{BET} of the clay samples extracted from the horizons B_2 and C_1 of the Eutric Planosol remains unchangeable but the surface area of the transitional pores (S_p) decreases after removal of the larger part of the organic matter by hydrogen peroxide (Tab.1).

Table 1. Structural-adsorption characteristics of clay fractions (particles < 2 μm), extracted from Eutric Planosol and Eutic Vertisol. 1 – initial sample; 2 –H_2O_2 treated; 3 –electro-dialysed; 4 – H_2O_2 + $Na_4P_2O_7$ treated; S_{BET} – specific surface area (Brunauer et al., 1938); S_p – surface area of the transitional pores (Kiselev, 1949); r – mean pore radius (Orr and Dalla Walle, 1959); d – distance between the flat-parallel layers (Innes, 1957); V_μ- micropore volume; V_o – maximum pore volume; V_p – volume of the transitional pores.

Soil / horizon / Sample No.			S_{BET}, m^2/g	S_p, m^2/g	r_p, Å	d, Å	Pore volume, $(cm^3/g)x10^2$			Organic carbon, %
							V_o	V_p	V_μ	
Eutric Planosol	A_1	1	31.3							1.88
		2	36.6							0.74
		3	41.8							2.01
		4	42.2	38.0	18.6	25	5.7	4.6	1.1	0.23
	B_2	1	85.3	61.0	14.8	30	7.1	5.2	1.9	1.34
		2	86.3	40.0	18.6	25	6.7	3.9	2.8	0.59
		3	105.8	83.0	14.8	25	10.4	8.2	2.2	1.57
		4	134.1	78.0	18.6	30	12.9	8.6	4.3	0.24
	C_1	1	81.4	37.0	18.6	25	8.2	5.4	2.8	0.56
		2	82.4	24.0	14.8	30	6.6	3.1	3.5	0.37
		3	103.2	73.0	18.6	30	10.8	8.4	2.4	0.64
		4	133.2	86.0	23.3	30	12.1	8.6	3.5	0.17
Eutric Vertisol	A_{pl}	1	90.0	16.0	18.6	25	6.3	2.3	4.0	2.24
		2	118.4	24.0	18.6	25	8.3	3.1	5.2	0.68
		3	119.7	36.0	14.8	25	9.0	4.4	4.6	2.49
		4	183.3	68.0	14.8	30	15.1	7.8	7.3	0.17
	B_1	1	94.5	10.0	18.6	30	5.5	0.7	4.8	1.75
		2	111.4	26.0	14.8	25	8.5	3.0	5.5	0.53
		3	129.3	49.0	14.8	30	9.7	5.0	4.7	1.94
		4	165.8	141.0	23.3	25	16.3	13.2	3.1	0.19
	C_1	1	131.0	26.0	14.8	30	10.0	4.4	5.6	1.81
		2	124.9	28.0	14.8	30	8.0	2.9	5.1	0.44
		3	125.8	24.0	14.8	30	8.0	2.7	5.3	1.02
		4	177.2	92.0	14.8	30	15.3	10.2	5.1	0.15

The compensation of this reduction is on account of a part of the micro-pores, not included in the calculation of S_p, but becoming available for the nitrogen molecules because of their unblockage after the humus removal. Indication for a similar redistribution gives also the fact that the total pore volume (V_o) decreases slightly on account of the meso-pores (V_p), while the volume of micro-pores (V_μ) increases.

S_{BET} for the sample isolated from the horizon A_1 of the same soil increases but the capillary condensation hysteresis is still slightly expressed. It is most likely that this is related to opening of relatively large voids between contacting kaolinic particles and fine-dispersive quartz, which dominate in this clay fraction. It can be assumed that a part of the macromolecules of the present humic substances is situated there.

Removal by H_2O_2 of the organic matter from the samples isolated from the horizons A_{plough} and B_1 of the Eutric Vertisol increases S_{BET} and the surface area of the meso-pores (S_p) (Tab.1). The total pore volume (V_o) increases also and it is on account of the volume of the meso-pores (V_p).

It is considered that the organic matter binds the individual clay particles in larger aggregates and at the same time a part of it is located on the surface of the particles. Complicated system of pores is formed in this way. As a consequence of the impact of H_2O_2 the larger part of the humus is removed and the result of the subsequent disaggregation is an opening of new surfaces (Fig. 4-6). This means that the treatment by hydrogen peroxide reflects on the total area of these two effects.

There is an opportunity for creating valence bounds between the humic substances and the lateral surfaces of the clay minerals for the samples isolated from the horizons of the Eutric Planosol where the soil reaction is severely acid (A_1 and B_2 horizons – Figs. 1,2). It is very likely that the attack with hydrogen peroxide is not sufficiently aggressive for their breaking and this reflects on the absence of change of the initial specific surface after this treatment. There are no conditions for creation of such a bond, the disaggregation is more complete and the deliberated surface is larger at the samples isolated from the horizons A_{plough} and B_1 of the Eutric Vertisol.

The specific surface area and the total pore volume increase sharply while the volume of the micro-pores remains almost unchanged after electro-dialysis of all the studied samples (Tab.1). This means that the meso-pores are the main bearer of the surface area after electro-dialysis. At this process, the fine-dispersive particles bound with the organic matter disaggregate completely and the cation bridges between the humic acids and the clay minerals are destroyed. This is explicable taking into consideration that the treatment is not connected with the direct affect on the organic matter but only disaggregation and probably dispersion of the available clay particles on account of the extracted cations.

After removal of the organic matter by $Na_4P_2O_7$+H_2O_2 (Figs.s 1-6), the distance between the adsorption and desorption branches of the isotherms decreases at all samples. This is an indication for equalization of the pore type and its approximation to the cylindrical form (Komarov, 1977). There is no suppress in the curves of desorption and their way goes down slowly with the decrease of the relative pressure, which is possible only for pores with all kinds of sizes. This is proved also by the strong dispersion around their average radius (Figs. 7-12). The surface area of the meso-pores increases strongly and approaches the values determined after electro-dialysis of the same samples. The strongest increase of the total pore volume (V_o) is after this treatment and it is mostly on account of the meso-pore volume (V_p) (Tab.1).

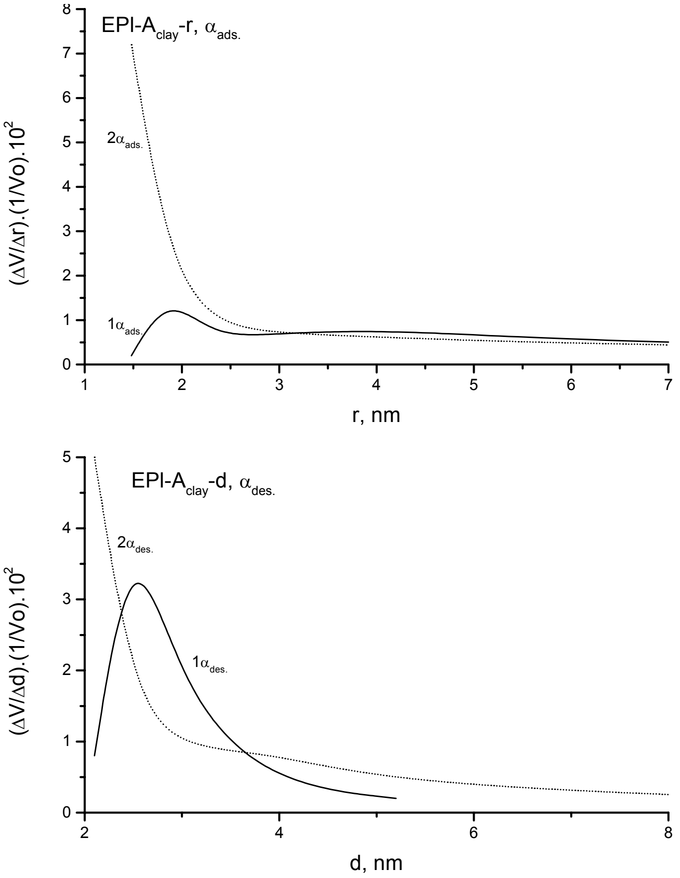


Fig. 7. *Pore-size distribution for < 2 µm clay fractions isolated from layer A of Eutric Planosol calculated by the method of Orr and Dalla Walle (r, $\alpha_{ads.}$); by the method of Innes (d, $\alpha_{des.}$). 1 – untreated; 2 – treated with H_2O_2; 3 – elecrtodialysed; ΔV – volume of the filled pores corresponding to Δr; Vo – total pore volume.*

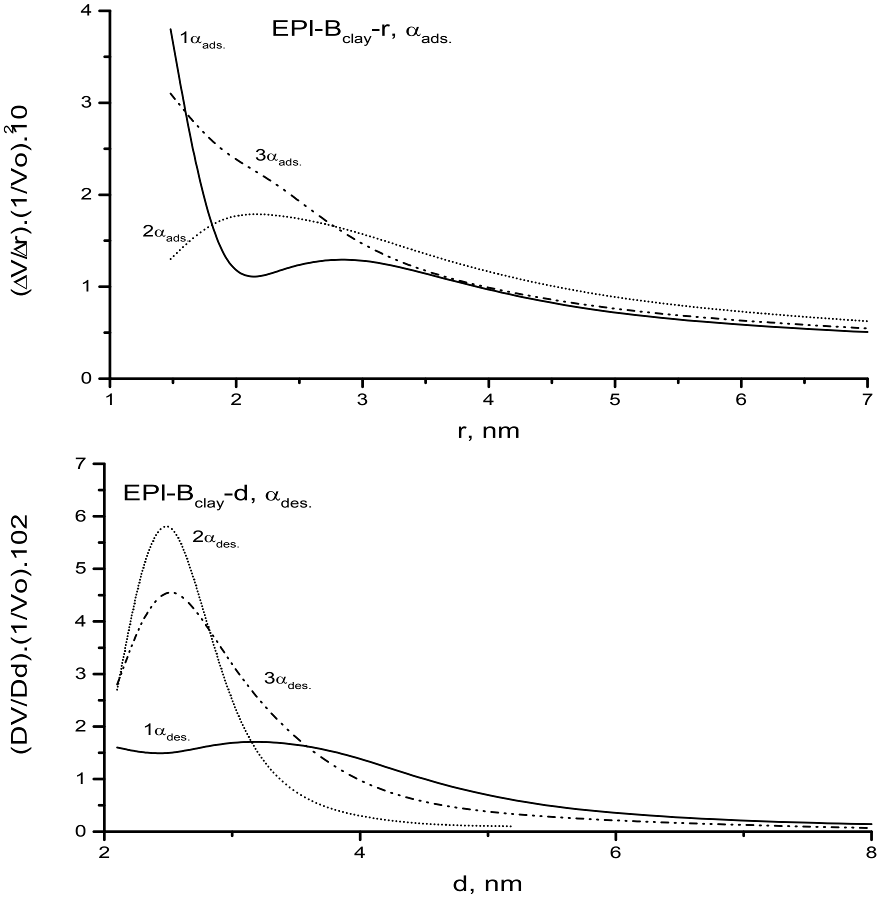


Fig. 8. *Pore-size distribution for < 2 μm clay fractions isolated from layer B of Eutric Planosol calculated by the method of Orr and Dalla Walle (r, $\alpha_{ads.}$); by the method of Innes (d, $\alpha_{des.}$). 1 – untreated; 2 – treated with H_2O_2; 3 – electodialysed; ΔV – volume of the filled pores corresponding to Δr; Vo – total pore volume.*

After electro-dialysis of the samples pre-treated by this method, the way of the curves becomes even steeper. The hysteresis decreases and the specific surface increases greatly. All these point to occurrence of extremely severe changes in the morphology of the studied subjects.

The analysis of the adsorption-desorption curves show that they are obtained by overlapping two types of isotherms with hysteresis (De Boer, 1958). The first hysteresis is of a type B, which corresponds to flat-parallel or bottle-shaped pores on the understanding that the radius of the voids (r_b) is larger than the radius of the necks (r_n): $r_b >> r_n$

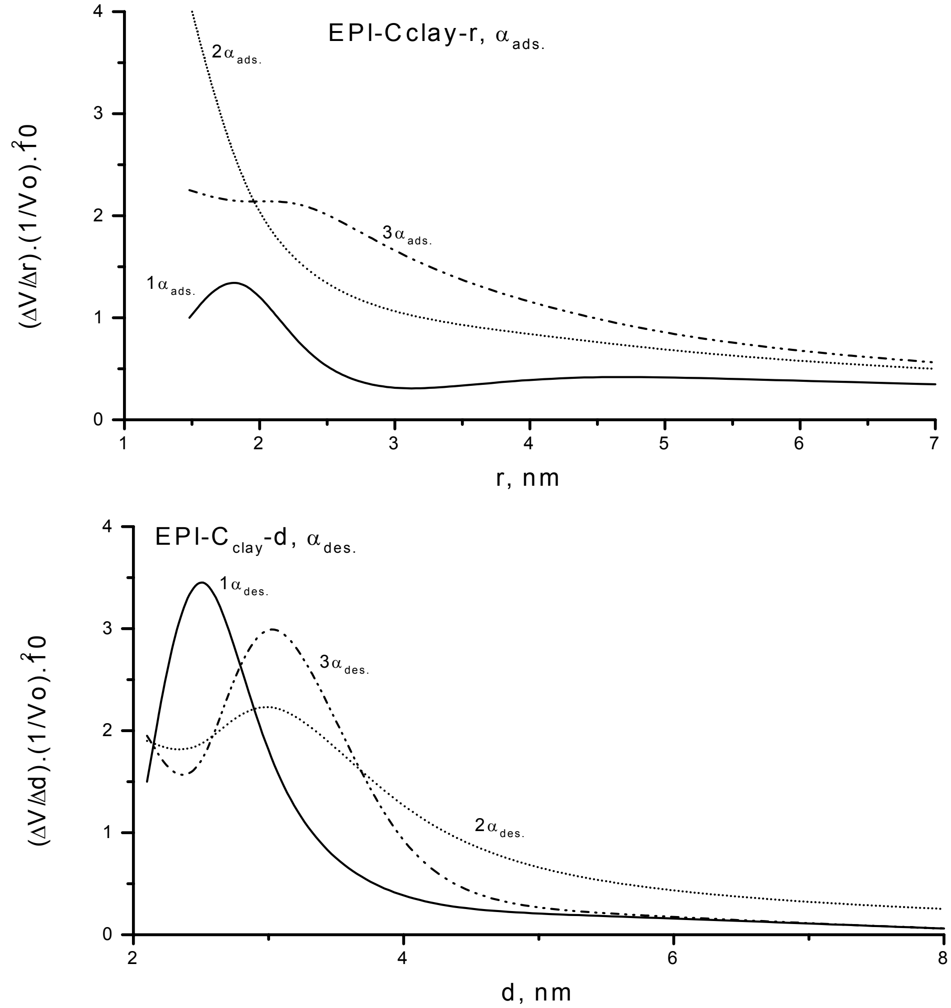


Fig. 9. *Pore-size distribution for < 2 μm clay fractions isolated from layer C of Eutric Planosol calculated by the method of Orr and Dalla Walle (r, $\alpha_{ads.}$); by the method of Innes (d, $\alpha_{des.}$). 1 – untreated; 2 – treated with H_2O_2; 3 – electodialysed; ΔV – volume of the filled pores corresponding to Δr; Vo – total pore volume.*

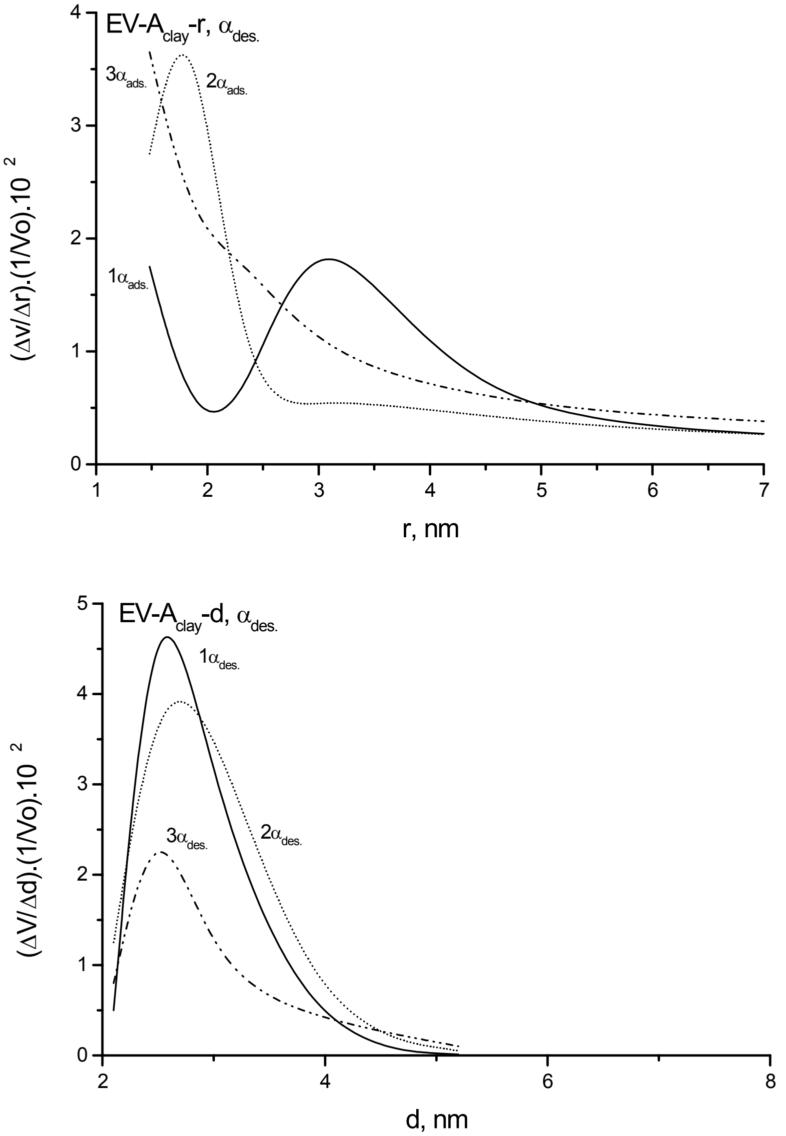


Fig. 10. *Pore-size distribution for < 2 μm clay fractions isolated from layer A of Eutric Vertisol calculated by the method of Orr and Dalla Walle (r, $\alpha_{ads.}$); by the method of Innes (d, $\alpha_{des.}$). 1 – untreated; 2 – treated with H_2O_2; 3 – electodialysed; ΔV – volume of the filled pores corresponding to Δr; Vo – total pore volume.*

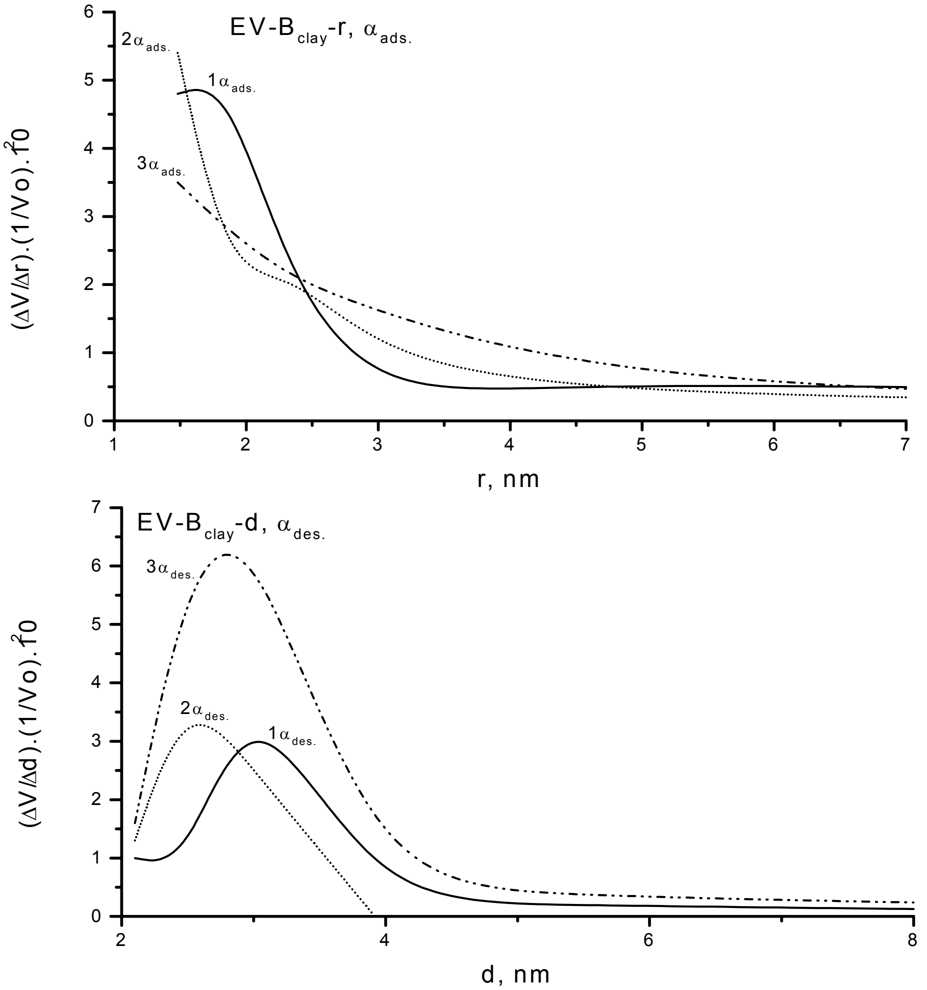


Fig. 11. *Pore-size distribution for < 2 μm clay fractions isolated from layer B of Eutric Vertisol calculated by the method of Orr and Dalla Walle (r, $\alpha_{ads.}$); by the method of Innes (d, $\alpha_{des.}$). 1 – untreated; 2 – treated with H_2O_2; 3 – electodialysed; ΔV – volume of the filled pores corresponding to Δr; Vo – total pore volume.*

It can be assumed that the presence of flat-parallel pores in the soils is due to the layered structure of the clay minerals. The second hysteresis is of a type E conditioned by the presence of cylindrical pores with 'constrictions' or bottle-shaped with reduced difference between r_b and r_n. Their presence can be explained by the origination of micro-voids between or in the walls of the lamellar pores.

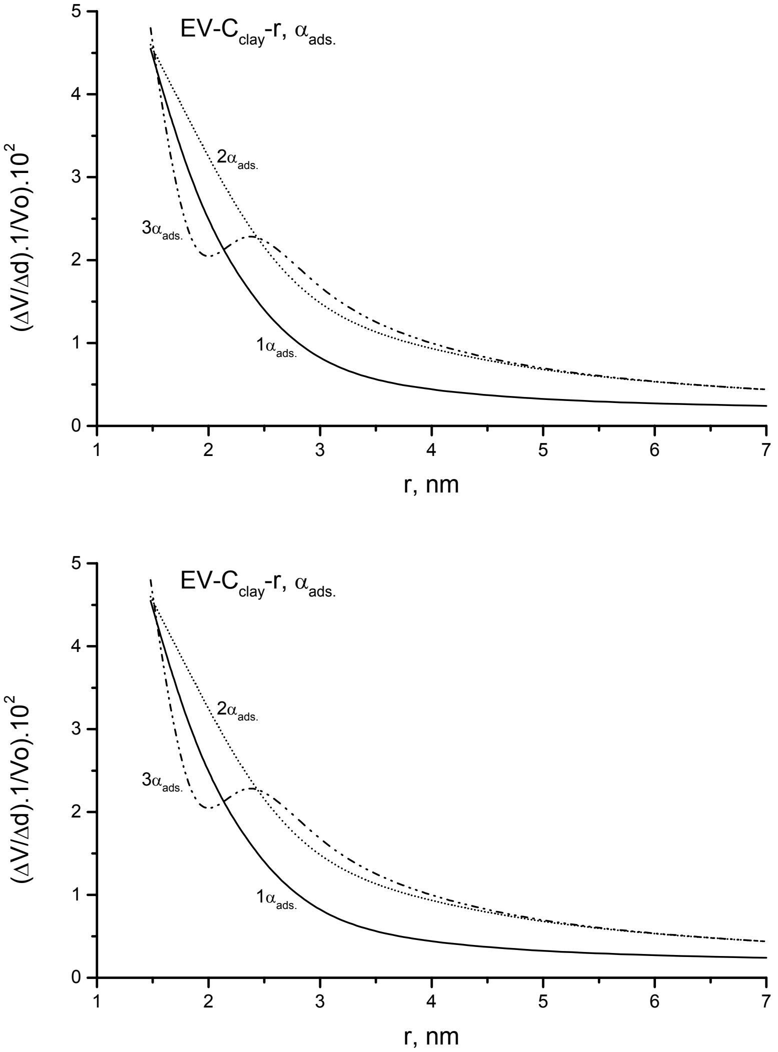


Fig. 12. *Pore-size distribution for < 2 μm clay fractions isolated from layer C of Eutric Vertisol calculated by the method of Orr and Dalla Walle (r, $\alpha_{ads.}$); by the method of Innes (d, $\alpha_{des.}$). 1 – untreated; 2 – treated with H_2O_2; 3 – electodialysed; ΔV – volume of the filled pores corresponding to Δr; Vo – total pore volume.*

And finally, it should be noted that the way of the desorption curves of the adsorption-desorption isotherms presented in Fig. 4 and Fig. 5 is anomalous as the adsorbed amount increases with the decrease of the relative pressure in the interval P/Po = 0.8 ÷ 0.6. One of the possible causes for similar anomalies is that different modifications in the structure of the clay minerals are possible during the adsorption measurements. That sort of changes has been observed in many cases during adsorption of water vapours on montmorillonite (Barrer and Mc Leod, 1954; Barrer and Reay, 1957). Their appearance at 77.4^{o}K is an interesting observation.

In this case is likely to take into consideration that the presence of clay minerals in the soil is in the form of a natural organic-mineral mixture, which components react differently and not simultaneously to applied impacts. During drying clay suspensions or pastes, for example, point contacts of cohesion come into being, corresponding to several atoms or one elementary particle (Rebinder, 1966). Colloid zones originate on the mineral surfaces in the presence of oppositely charged colloid forms of polyvalence cations and the contact would modify its character. Simultaneously, the openings between the contacting particles form a system of pores` which can modify its condition in the course of different adsorption processes. Hence, the clay minerals cannot be considered as inert during adsorption (Yets, 1964; Tarasevich and Ovcharenko, 1975). The way of the obtained isotherms would be affected by factors as:

- Opportunity for modification of the between-package space of adsorbents with mobile crystal lattice;
- Between-crystal swelling;
- Destroying point and colloid contacts between the particles;
- In simultaneous and unequal reaction of the components to these processes during adsorption.

The problems grow at structural-adsorption studies on humic preparations. According to Orlov (1974) compaction takes place during drying of humic acids and the organic particles become roentgen-amorphous as a consequence of the modification in their configuration. The electron-microscopic analysis of samples from humic preparations isolated from the studied soils and dried at different conditions (on air, in vacuum and under lyophilization at -50^{o}C) shows certain arrangement and absence of compaction for the lyophilized preparations (photographs 1a, 1в and 1c). In the samples dried on air or under vacuum but without freezing, there are dense spots, which are typical for the ordinarily observed soil organic matter.

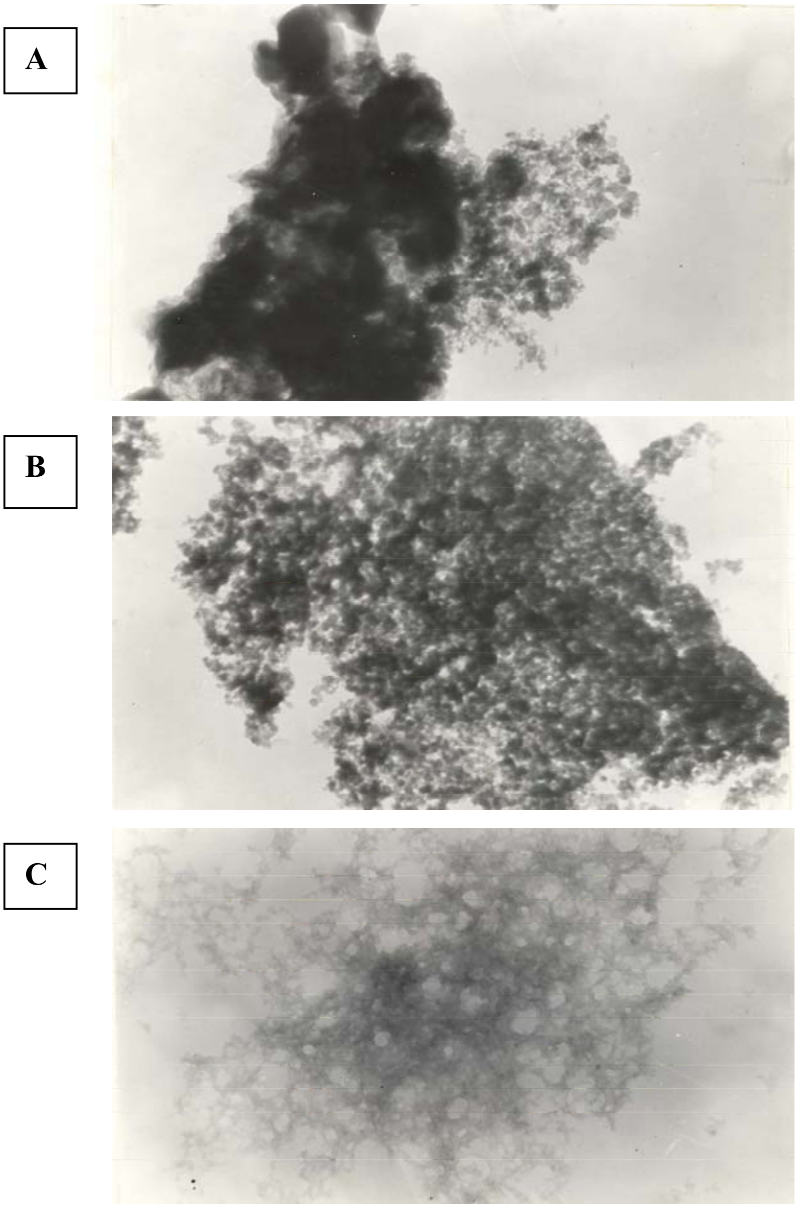


Fig. 13. *Electron-microscopic photographs of humic acids after drying: A – on air; B – under vacuum; C – under freezing*

It should be also noted that the simple static idea about the molecular structure is not applicable for the macromolecules of the humus substances. This term should be adopted in a broader sense, including not only the process of their formation but also their diverse dynamic behaviour. It is no accident but it is an integral property of the bio-molecule and this determines its dynamic structure and biological function. The more important sterical peculiarities of these highly-molecule formations are connected with the flexibility of their chains. It decreases with the increase of the number of polar groups and with the increase of the size of the spatial net. This property is extremely important as far as it enables development of 'clathrate' compounds, in which the spatial configuration of the molecules allows their mechanical binding. The elasticity and the extremely high activation of the organic fragments facilitate the formation of stable adsorption-solvate layers on the surface of the mineral colloids building the organic-mineral kernel of the soil adsorbent. It should be taken into consideration also that the carbon-containing sorbents have micro-porous structure. The narrowing, commensurable or slightly wider than the cross-section of the adsorptive molecule, behave as if they guard the entrances to the pore voids and their passage is severely embarrassed. This way, the establishment of the adsorption equilibrium is retarded, which causes problems for the structural-adsorption measurements.

All these justify the investigations of the clay fractions of the selected soils, with extraction accomplished without application of chemical treatments (Aydinyan, 1966). The reasons for appearance of the anomalies in the way of the desorption branch of the isotherms are analyzed more thoroughly in one of the following parts of the study.

CONCLUSIONS

The observed changes in the structural-adsorption characteristics of the clay fractions from the studied soils confirm the established dependence of the applied treatments from:

- The amount and the dominating type of the clay minerals;
- Humus content;
- The manner of bonding in the organic-mineral associations.

The additionally obtained information at this stage of the studies can be generalized as follows:

1. The soil adsorbent of the studied soils can be referred to the sorbents with pronounced meso-porous character. Its heterogeneous transitionally-porous structure is a reflection of the dominant component in the composition of the primary organic-mineral matrix – the clay minerals. Their porous structure is built from relatively larger flat-parallel pores. The established presence of more narrow pores is likely to be caused by the existence of micto-voids between or in the walls of the lamellar pores.

2. in the structure of the soil adsorbent, three differently stable fractions of the humus substances can be distinguished, which sensibility to the applied treatments depends on their strength of binding in the organic-mineral association:

- HS_{clay} – humus substances, likely to be included in the primary organic-mineral matrix ($PM_{HS\text{-}clay}$), which is not affected by the applied treatments.

The stability of this primary clay-humus bond is likely to be a consequence of development of adsorption-solvate layer with high density on the surface of the clay minerals at the initial stages of humus-formation in the soil. The dehydrating action of the existing polyvalence cations and the direct phase contacts in absence of liquid layers add a significant durability and irreversibility at destroying of these condensation structures.

- $HS_{int.}$ – humus substances enriched with cyclic-kernel fragments included in the composition of the internal layer ($L_{int.}$), bond directly with the organic-mineral kernel ($PM_{HS\text{-}clay}$). It is likely that this increases its stability towards treatment with H_2O_2, while the electro-dialysis and the treatment by $H_2O_2 + Na_4P_2O_7$ are sufficiently aggressive to breaking its specific bond with $PM_{HS\text{-}clay}$.

The high elasticity of the organic poly-molecular elements enable more dense phase contacts with the modified surfaces of the clay minerals while the presence of polyvalence cations facilitates the formation of relatively shortened bridge bonds. Their stability increases at 'clathrate' disposition of these ions in conformation mobile voids of the humus poly-molecules enriched by cyclic structures, which is not impossible because of their strongly expressed humic character.

- $HS_{back.}$ – humus substances of fulvic type, which are connected by cation bridge bond with the internal layer ($L_{int.}$) and form the external layer ($L_{back.}$) of the soil adsorbent (SA). The availability of large number of functional groups in their long-chain molecules and the presence of polyvalence cations facilitates the bonding of individual organic-mineral units in more compact aggregates by bridge mechanism and flocculation. It should be assumed that this bond is more stable and its strength approaches that of $L_{int.}$ - $PM_{HS\text{-}clay}$, but the applied in this study treatments cannot distinguish between them.

It should be noted that both bonds are relatively weak and sensible to chemical or microbial attack because of the point character of the structure-formation and they are unstable at treatment with hydrogen peroxide. The main reason for the absence of dense between-phases contact for them is the lower elasticity of the organic chains in this layer compared to their organic analogue in the internal one. This gives rise to conformation heterogeneity of the contacting phases and reduces the strength of the bond between them. Opening of the transitional layer of the soil adsorbent follows from its destroying as well as additional disaggregation, which reflects on the total area of the surfaces opened by these two effects.

REFERENCES

Anderson, R., 1972. Experimental methods for studying the catalysis. Publ. “Mir”, M, p.480. (Ru)

Atanassov, Iv., 1977. Weathering and evolution of mineral part of the soils in Bulgaria. D. Sci. Thesis, Higher Agric. Inst., Sofia, p. 566. (Bg)

Atanassov, Iv., D. N. Dimitrov, 1976. Distribution of the fine-dispersive minerals within the profile of light-grey gleyic soils. Soil Science and Agrochemistry, (XI) 3:17-25. (Bg)

Aydinyan, R. H., 1966. Accelerated method for extraction of soil clay and colloids using super-centrifuge. Agrochemistry, 6:151-156. (Ru)

Bolshakov, V., 1978. Application of the method of electro-dialysis for soil studies. Proc. Soil Sci. Inst. Dokuchaev W.W., M. (Ru)

Brunauer, S., L. S. Deming, W. S. Deming, E. J. Teller, 1940. Theory of Van der Waals adsorption of gases. J. Am. Chem. Soc., 62 (7):1723:1732.

Brunauer, S., P. H. Emmet, E. Teller, 1938. Adsorption of gases in multimolecular layers. Journal of American Chemical Society, 60, 309 – 314.

De Boer, J. H., 1958. The Structure and Properties of Porous Materials, Butterworth, London, 68 pp.

Dubinin, M. M. 1965. Modern State of the Theory of Gas and Vapour Adsorption by Microporous Adsorbents. Pure and Appl. Chem., 10: 309-321.

Dubinin, M. M., 1970. Fundamental problems of the physical adsorption theory. Proc. I All-Union Conf. Theoretical Probl. Adsorption. Publ. “Nauka ”, M., p.476. (Ru)

Dubinin, M. M., 1972. Adsorption and porosity. Proc. All-Union Conf. Theoretical Probl. Adsorption. Publ. “Nauka ”, M., p.360. (Ru)

Dubinin, M. M., E. G. Zhukovskaya , E. D. Zaverina, I. E. Neymark, R. Yu. Sheinfain. 1960. Study on the adsorption of vapours of adsorbents with inhomogeneous surface. Proc. AS USSR, OChSci, 4:588-598. (Ru)

Ganev, S., A. Arsova, 1980. Methods for determination of the strongly acidic and weakly acidic cation exchange in soils. Sofia, Soil Sci. and Agrochemistry,15 (3): 22-33 (Bg).

Gregg, S. J., K. S. W. Sing, 1967. Adsorption, Surface Area and Porosity. Academic Press, London and New York, p.304.

Innes, W. B., 1957. Use of Parallel Plate Model in Calculation of Pore Size Distribution. Anal. Chem., 29: 1069-1073.

Jackson, M. L., 1958. Soil Chemical analysis, New York:Prentice-Hall, p.498.

Kiselev, A. V., 1958. The Structure and Properties of Porous Materials. Ed. D. H. Everett, F. Stone, London, p 195.

Komarov, V. S, 1977. Adsorbents and their properties, Publ. “Nauka I tehnika”Minsk. 248 p. (Ru)

Kononova, M. M., 1966. Soil organic matter. It's nature, it's role in soil Formation and Soil Fertility. 2nd English Ed., Pergamon Press Inc., Elmsformd M.V., 544 pp.

Kozhuharov, M., S. N. Alyoshin, 1962. On the progress of separation of exchangeable bases and anions from some Bulgaria soils using electro-dialysis. Higher Agric. Inst. G. Dimitrov, Proc. Agronomy Faculty*, v.* 11, 105-122. (Bg)

Orlov D. S., 1974. Soil humus substances. Univ. of Moscow Ed., Moscow, 333 pp. (Ru).

Orr, C., J. M. Dalla Walle, 1959. Fine particle measurement, Macmillan, London, p.846.

Ostrikov, M. S., 1960. Natural Mineral Sorbents, Publ. AS USSR, Kiev: p.172. (Ru)

Raytchev, T., 1997. Kinetics of the desorption of cations. II. Desorption of exchangeable calcium depending on humus quality in the soil, Soil science, Agrochemistry and Ecology, Sofia, vol. XXXII, 4:37-39. (Bg).

Raytchev, T., R. Toncheva, 1997. Kinetics of the desorption of cations. I. A mathematical model testing, Soil science, Agrochemistry and Ecology, Sofia, vol. XXXII, 4:34-36. (Bg).

Raytchev, T., 1996. Influence of organo-mineral interactions on colloid-chemical state of the soil adsorbent. D. Sci. Thesis, "N. Poushkarov" Inst., Sofia, 161 pp. (Bg).

Rebinder, P. A., 1966. In: "Physico-chemical mechanics of disperse structures". Publ."Nauka", M., p. 400. (Ru)

Tarasevich, Yu. I., F. D. Ovcharenko, 1975. Adsorption of Clay Minerals. Publ. "Naukova dumka", Kiev: p.352. (Ru)

Yets, D., 1964. In: "Catalysis. New physical methods and studies ", Publ. "Mir", M.: p.372. (Ru)

ON THE ANOMALOUS SHAPE OF LOW-TEMPERATURE NITROGEN ADSORPTION ISOTHERMS OF < 2μm CLAY FRACTIONS ISOLATED FROM SOILS

***Mehandjiev D.*[1]*, Raytchev T.*[2]**
***Sokolowska Z.*[3]*, Hajnos M.*[3]**

[1] Institute of General and Inorganic Chemistry, Bulgarian Academy of Science, Sofia, Bulgaria
[2] N. Poushkarov Institute of Soil Science, 7 Shosse Bankja Str., 1080 P.O. Box 1369, Sofia, Bulgaria
[3] Institute of Agrophysics, Polish Academy of Sciences, 4 Doswiadczalna Str., P.O. Box 201, 20-209 Lublin, Poland

Abstract

It is shown that the methods of pore – size distribution determination should be applied cautiously to soil fractions. The presence of a natural mixture of minerals and other substances is the cause of different reactions of some components at different moments of adsorption. Attention has been paid to the effect of organic substances in soils on the anomalies in the desorption curves. It should be taken into account that the possible adsorbent changes during the measurement could affect the experimental results. Attempts have been made to elucidate the mechanism of some of these changes and it is concluded that the pore – size distribution should be calculated from both branches of the adsorption isotherms especially for adsorbents with an expanding crystal lattice, to which most clay minerals belong.

INTRODUCTION

The sorption, capillary and gravitational forces acting on the surface and in the bulk of soil particles change with varying the distance between them, the potential field between the colloidal particles and that between their aggregates being of different values and nature. This produces physical, and above all, energy inhomogeneity of the pore space. The pore structure affects the surface accessibility, activity and selectivity to sorption processes. It is evident that the study of the processes taking place on the surface of soil particles should begin with the determination of the surface area and the porous structure. The peculiarities of soils, however, make it sometimes difficult to obtain detailed information in this respect.

The specific surface area is mostly determined by means of low – temperature nitrogen adsorption (Brunauer et al., 1938). This method is applicable with adsorption isoterms types II or IV of BDDT (Brunauer et al., 1940). Therefore, with microporous samples (radius < 15Å) for which I type isotherms are obtained (Langmuir isotherms) the results obtained by the BET method are not sufficiently exact (Greeg and Sing, 1967). The pore – size distribution can be determined by some of the existing methods (Innes, 1957; Orr and Dalla Walle, 1959). It is interesting to know which branch of the isotherm (i. e. the adsorption or desorption one) should be used for calculating the pore – size distribution. It is a well – known fact that some structural changes may occur during the adsorption process in soils and especially in clay minerals because of the above peculiarities. Such phenomena are observed in many cases of water vapour adsorption on montmorillonite (Barrer and Mc Leod, 1954; Barrer and Reay, 1957). In fact, these effects could appear, to a smaller extent, with adsorption of other substances and even with low – temperature nitrogen adsorption which is used, as already mentioned, for determining specific surface areas and pore – size distributions. For this reason, the purpose of the present paper was to study the nitrogen – adsorption isotherms of soils and to establish how the character of these isotherms and the determination of the pore – size distribution are affected by the removal of the organic substance and the cation depletion.

MATERIALS AND METHODS

Samples of clay fractions obtained by the method of Aidinyan (Aydinyan, 1966) from the A and B layers of leached smolnitza (Eutric Vertisol) were used in the study. The organic substance was removed by treatment of the samples with H_2O_2 during heating on a water bath. The exchange ions were removed by electrodialysis (Kozhuharov and Alyoshin, 1962). However, this experiment was to be carried out carefully since the clay minerals are easily decomposed at high current densities (Eitel, 1962).

The structural and adsorption characteristics of the investigated samples were determined from the isoterms obtained by low – temperature adsorption of nitrogen:
S_{BET} – specific surface area, m^2/g (Brunauer et al., 1938)
r – radius of bottle-shaped pores calculated by adsorption curve, Ǻ (Orr and Dalla Walle, 1959)
d – radius of slit-shaped pores calculated by desorption curve, Ǻ (Innes, 1957)
V_o – total pore volume, $cm^3.g^{-1}$
ΔV – change of the filled pore volumes corresponding to Δr.

RESULTS AND DISCUSSION

Figures 1 and 2 show the results obtained from adsorption studies (each isotherm is shifted along the abscissa by $P/P_0 = 0.5$). N°1 in all figures corresponds to the initial sample isolated from the corresponding soil layer; N°2 denotes the sample after treatment with H_2O_2; N°3 represent the electrodialyzed samples. All isotherms show a clearly expressed hysteresis.

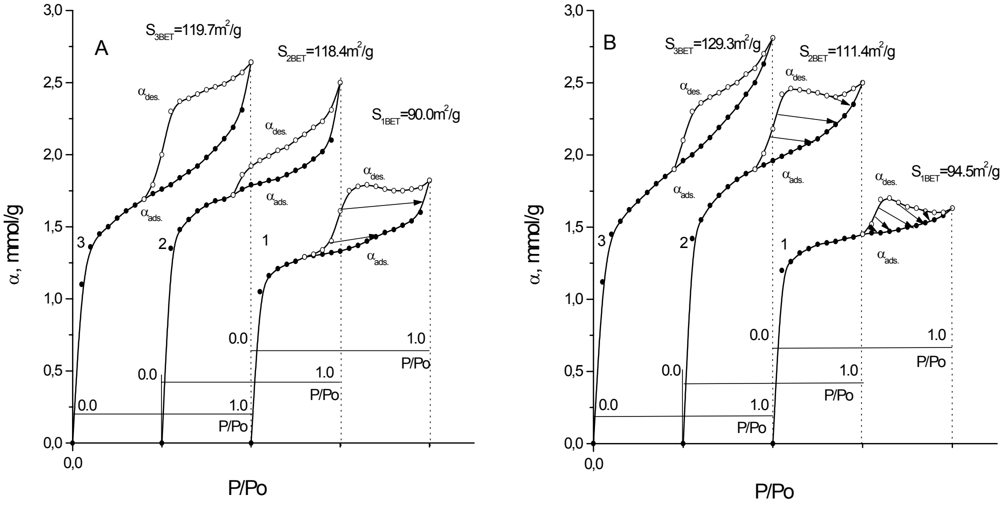


Fig. 1. *Low-temperature nitrogen adsorption-desorption isotherms for < 2 μm clay fractions isolated from layer A (A) and layer B (B) of Eutric Vertisol (each isotherm is shifted along the abscissa by P/Po = 0.5); α – adsorbed amount, mmol/g; 1 – untreated; 2 – treated with* H_2O_2; *3 – electodialyzed; ΔV – volume of the filled pores corresponding to Δr; Vo – total pore volume.*

Analysis of the sorption curves shows that they represent a combination of two types of isotherms (De Boer, 1958) with hysteresis. This is the so - called B type hysteresis which corresponds to slit- or bottle-shaped pores when the difference between the radius of the bottle body (r_b) and that of its neck(r_n) is very large,

$$r_b \gg r_n . \qquad (1)$$

We shall assume that this is due to the presence of parallel flat pores in the soils. The second type of hysteresis, type E, is due to irregular tubular pores or to bottle-shaped pores with small differences between r_b and r_n. The adsorption isotherms in Fig.1A (N°1) and Fig.1B (N°1 and N°2) have an interesting anomalous shape. Figure 1A (sample N°1) and Fig.1B (sample N°2) show an increase in the adsorbed amount with decreasing relative pressure, P/P_0 from 0.8 to 0.6, after which the desorption branch has an almost vertical course. In Fig.1B (sample N°1) the adsorbed amount increases with decreasing P/P_0 and becomes larger than the amount at P/P_0 =1.0.

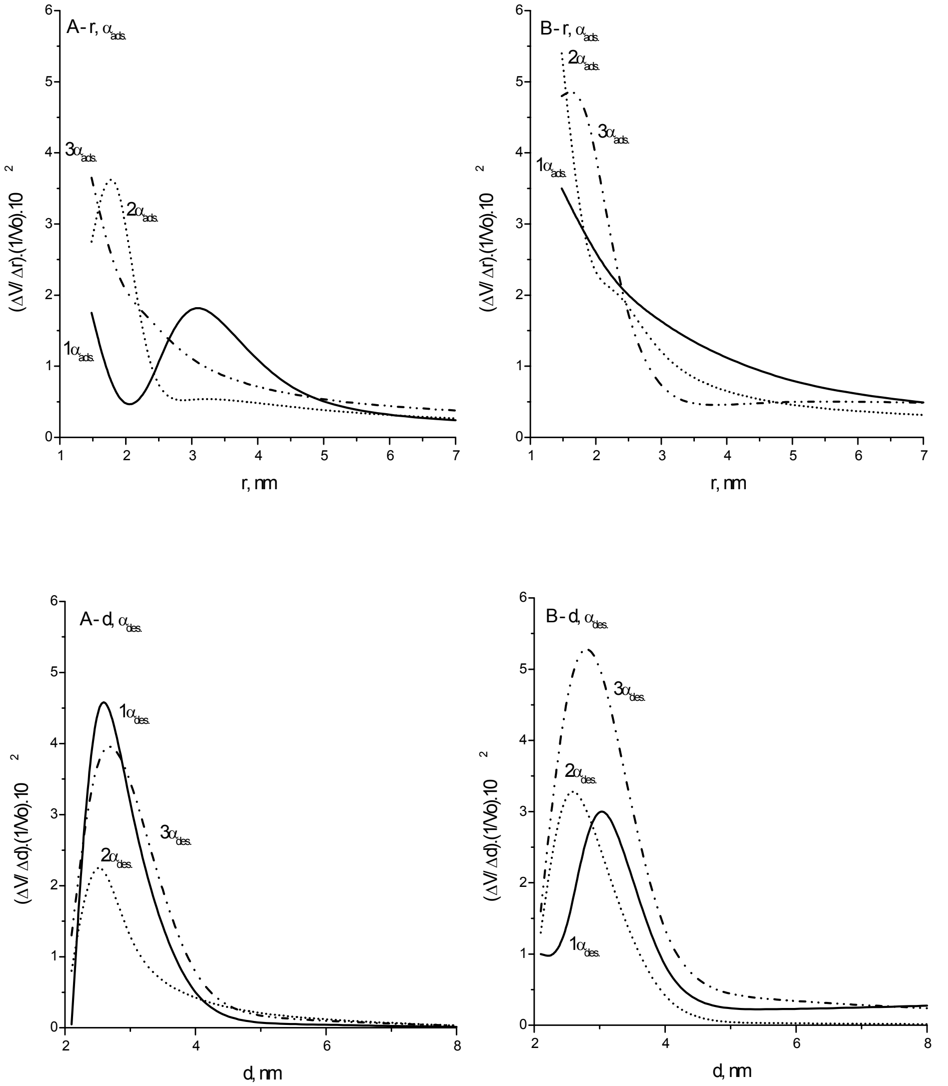


Fig. 2. Pore-size distribution for < 2 μm clay fractions isolated from layer A (A) and layer B (B) of Eutric Verisol calculated by the method of Orr and Dalla Walle (r, $\alpha_{ads.}$); by the method of Innes (d, $\alpha_{des.}$).1 – untreated; 2 – treated with H_2O_2; 3 – electodialyzed; ΔV – volume of the filled pores corresponding to Δr; Vo – total pore volume.

These anomalies can be explained as follows. With all methods of pore - size distribution calculations it is assumed that this distribution, as well as the surface area of a given sample, remain constant during adsorption and desorption. A given point of the adsorption or desorption branch of the isotherm will be then described by the following equation:

$$V_a = \sum_{i=1}^{k} V_i - t_k \sum_{i>k} S_i \tag{2}$$

where V_a is the adsorbed volume, S_i is the surface of pores with a radius larger than r_k , V_i is the volume of the pores which have a radius smaller than or equal to r_k.. According to the Kelvin equation, one obtains for r_k

$$r_k - t_k = \frac{A}{\lg P/Po} . \tag{3}$$

Here, A is a constant which depends on the pore forms, the molar volume (V),and the surface tension (γ); t_k is the adsorption layer thickness at a relative pressure P_k/P_0 ; t is calculated using the formula

$$t = \sigma \left[\frac{5}{2.3031 \lg P/Po} \right]^{1/3} , \tag{4}$$

where σ is the mean thickness of the layer of adsorbed molecules (Shull, 1948).

If it is assumed that with increasing the thickness of the adsorption layer the pore radius changes, i.e. that there is a correlation of the kind

$$r = f(t) \tag{5}$$

and if r increases with increasing t,and vice versa, r decreases with decreasing t , then during adsorption r will increase with increasing P/P_0 because t will increase (formula 4). This will retard the process of capillary condensation. During desorption with decreasing P/P_0 , t and r will decrease. This may lead again to a process of capillary condensation in pores which have been emptied at higher relative pressures but whose r has decreased according to equation (Orr and Dalla Walle, 1959). In this case, there will be an anomalous change in the desorption branch of the isotherm which will be analogous change experimentally obtained with the samples studies by us (Fig.1A - *1*; Fig.1B - *2*). An anomaly of the show in Fig.1B - *1* is observed when the surface changes (i.e. new surface areas appear) during adsorption or desorption. Therefore, the anomalies observed should be due to a change in the pore - size distribution and in some cases, to a change of the surface area during the adsorption measurement. Such change are possible in soils. However, it is interesting that in this case they occur at an adsorption temperature of 77.4 K.

As is known, in montmorillonite an octahedral aluminium layer is sandwiched between two tetrahedral silicon layers, all of them forming together a three - layer structure unit (layer unit).The porous structure of the minerals forming a soil is due to micropores between the layer units and macropores formed by the spaces between the particles (each particle consisting of several layer units). As the distance between the micropores is smaller than 15 Å, and the anomalies observed concern macropores (P/P_0=0.6 - 0.8), the changes should occur in the latter.

We consider the following physical explanation as the most probable one. A layer, *t*, is formed on the surface during adsorption. As a result of interaction with the surface, this layer disturbs the interactions between the particles which leads to an increase of the distances between them, and to the appearance of new surface areas. The effect is reversible, which is confirmed by the scanning of the adsorption hysteresis (Fig.1A, curve *1*,and Fig.1B). Hence,one may conclude that interactions are of a physical and not a chemical character,which is in agreement with the physical character of nitrogen adsorption at 77.4 K. Barer, McLeod and De Boer have established that in the space between two parallel plates which are not connected with each other, no meniscus can be formed before the vapour pressure, *P*,has attained the standard isotherm for the same substance with the also be a cylindrical meniscus on the desorption branch of the isotherm and for this reason the distance, *d*, between the plates can be calculated for each P/P_0 using equation

$$\ln\frac{P}{Po}=\frac{2\gamma V}{d_k RT}, \qquad (6)$$

where $d_k = d - 2t$.

Thus, with evaporation of the liquid, the plates will gradually come near to each other, and the values of *d* and P/P_0 will decrease. However, the distance cannot decrease below a certain minimum value. In our case the steep course of the desorption branch appears at P/P_0 =0.6 which corresponds to a distance between the plates d = 23.3 Å.

Some workers (Barrer and Mc Leod, 1954; Barrer and Reay, 1957) have studied the adsorption of nonpolar substances on montmorillonite and assumed that the desorption branch of the hysteresis is due to capillary evaporations of the adsorbate from the space between the plate - shaped particles,whose orientation is determined by the forces of surface tension in the tixotropic structure. After that, the adsorbate quickly evaporated which is confirmed by the vertical part of the desorption branch. According to Lippens, if the plates cannot move independently and the space between them is fixed, the polymolecular adsorption layer will be formed according to the standard curve up to a definite P/P_0 determined by the distance between the plates.

Figure 3 shows the value of the parameter *t*, calculated from the experimental data for the different samples and the theoretical curve calculated according to formula 4.

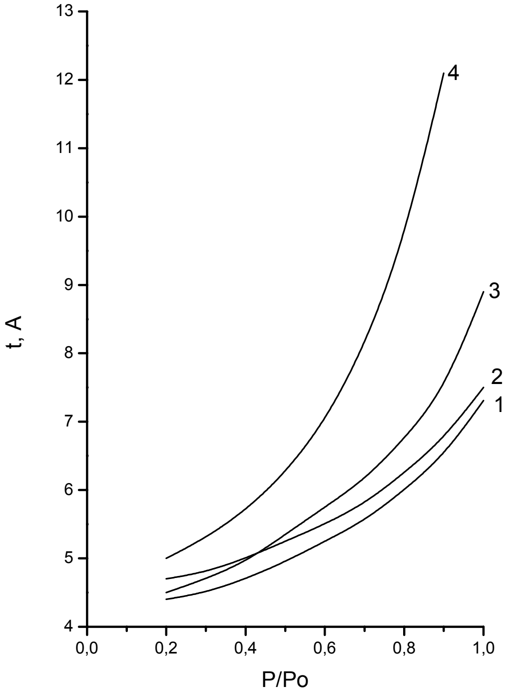


Fig. 3. *Dependence of the thickness, t, of the adsorbed layer on relative pressure of < 2μm clay fractions isolated from Eutric Vertisol: 1 – untreated; 2 – treated with H2O2; 3 – electrodialysed; 4 – theoretical curve calculated according to formula (4).*

It is evident that there is no good agreement between the experimental and the theoretical curves. This can be due to that no t layer, such as that formed on other adsorbents appears on the samples under investigation or that the formation of the corresponding number of layers is hindered in some way. It can be assumed that the rule for the t curve (Aylmore and Quirk, 1967; Paterson, 1977) is valid for clay minerals as well. On this basis, the second possibility seems more probable. Indeed, if the experimental data are presented in coordinates Vi - ti, where Vi is the adsorbed volume, and ti, the theoretical value, the dependencies shown in Fig. 4 are obtained.

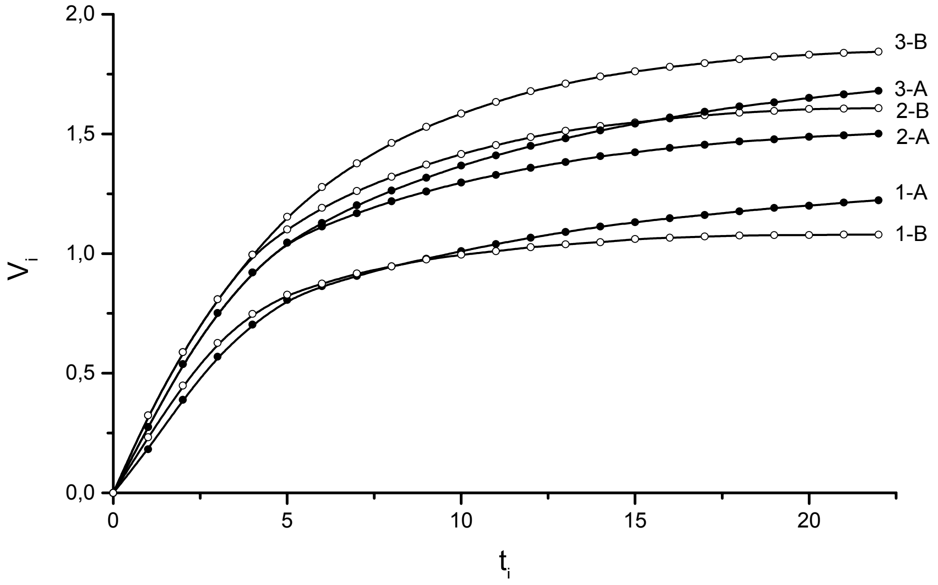


Fig. 4. *Dependence of the total volume (Vi) of adsorbed nitrogen on the thickness (t_i) of the adsorbed layer of < 2μm clay fractions isolated from layers A and B of Eutric Vertisol: 1 – untreated; 2 – treated with H_2O_2; 3 – electrodialyzed.*

Obviously, curves bent downwards are obtained instead of the expected straight lines. The same kind of curves are obtained with parallel flat pores in which the usual number of adsorption layer cannot be formed due to the narrowness of the pores (Komarov, 1977). This means that the pores are filled before the beginning of capillary condensation. Therefore, the porous structure of the soil samples under investigation is due to parallel flat pores and to narrow pores formed by the space between the particles begin in contact with one another and the space between the layer units. The sizes of all these pores depend on the adsorbed amount and this determines the anomalous shape of the adsorption isotherms. During adsorption, the smaller pores are filled. Then during desorption the liquid in the slit - shaped pores, which closes the smaller pores,should evaporate. In this case, the pore - size distribution, as determined from the adsorption branch, will give the size distribution of the narrow pores whereas the desorption branch will give the distribution of the distances between the slit - shaped pores.

Figures 2A and 2B show the distribution curves of the pore size. The calculation was made for the desorption branch by the method of Innes (Innes, 1957), whereas the method of Orr and Dalla Walle (Orr and Dalla Walle, 1959) was used for the adsorption branch. We proceeded from the fact that desorption occurs in parallel flat pores whereas adsorption takes place on cone-shaped and other pores. The distribution curves obtained confirmed our assumption about the soil structure. As a result of adsorption, the narrower pores (smaller than 15 - 20 Å) are filled. They form a relatively small part of the total pore volume. With desorption, information is obtained on the distance between the parallel flat pores which vary from 30 to 40 Å. These results are in agreement with the data of Aylmore and Quirk (Aylmore and Quirk, 1967). We consider the information obtained from the desorption peak to be more reliable. However, the possibility of changes in the structure during adsorption should also be taken into account.

Let us consider the effect of H_2O_2-treatment and electrodialysis on the shape of the adsorption isotherms and their anomalies. The latter are observed only in the presence of organic substance. After its partial removal, the anomalies decrease or completely disappear. The same happens after electrodialysis of the samples. In view of the fact electrodialysis does not remove the organic substance but causes disaggregation and dispertion of the particles, we can assume that the organic substance in the soil acts as "lubricant" which facilitates the movements of the clay particles in the separate aggregates. On the whole, the adsorbent cannot be considered inert during the process of adsorption (Balley et al., 1970; Yets, 1964; Kononyuk et al., 1972). This is valid especially for soils and fractions for which intercrystalline swelling (Barrer and Reay, 1957; Barrer et al., 1953) or intercrystalline swelling with destruction of the points of contact between the particles is possible (Rebinder, 1966). As a result, new adsorption centers appear. The presence of a natural mixture of various minerals and other substances will lead to different reactions of the components at different moments of adsorption.

The present study shows that the methods of determination of the pore - size distribution should be applied very carefully to the investigation of soils and soil fractions. In each separate case there should be a special approach to the experimental results which means that the possible change in the adsorbent during the measurement should be taken into account. Our study of the mechanism of these changes makes us assume that the pore-size distribution should be calculated using both branches of the adsorption isotherms especially in cases of adsorbents with an expanding crystal lattice, to which the clay minerals belong.

REFERENCES

Aydinyan, R. H., 1966. Accelerated method for extraction of soil clay and colloids using super-centrifuge. Agrochemistry, 6:151-156. (Ru)

Aylmore. L. A. G., Y. P. Quirk, 1967. The micropore size distribution of clay mineral systems. Soil Sci., 18: (1):1-17.

Balley, A., A. Cadenhead, D.H. Davies, D.H. Everett and A.J. Miles, 1970. Low pressure hysteresis in the adsorption of organic vaporous by porous carbons. Trans Faraday Soc., 67: 231-243.

Barrer, R. M., D. M. Mc Leod, 1954. Intercalation and sorption by montmorillonite. Trans Faraday Soc., 50 : 980-989.

Barrer, R. M., J. Drake, T. V. Whittam, 1953. Sorption of gases and vapors by K benzenesulfonate. Proc. Roy. Soc., 219A: 32-53.

Barrer, R. M., Y. S. S. Reay, 1957. Sorption and intercalation by methyl-ammonium montmorillonites. Trans Faraday Soc., 53: 1253-1261.

Brunauer, S., L. S. Deming, W. S. Deming, E. J. Teller, 1940. Theory of Van der Waals adsorption of gases. J. Am. Chem. Soc., 62 (7):1723:1732.

Brunauer, S., P. H. Emmet, E. Teller, 1938. Adsorption of gases in multimolecular layers. Journal of American Chemical Society, 60, 309 – 314.

De Boer, J. H., 1958. The Structure and Properties of Porous Materials, Butterworth, London, 68 pp.

Eitel, W., 1962.The Physics of the Silicates, Chicago, Illinis, Univ. of Chicago Press, 17. 1592.

Gregg, S. J., K. S. W. Sing, 1967. Adsorption, Surface Area and Porosity. Academic Press, London and New York, p.304.

Innes, W. B., 1957. Use of Parallel Plate Model in Calculation of Pore Size Distribution. Anal. Chem., 29: 1069-1073.

Komarov, V. S, 1977. Adsorbents and their properties, Publ. “Nauka I tehnika”Minsk. 248 p. (Ru)

Kononyuk, V. F., A. I.Saharov, M. M.Dubinin, 1972. About the change of the linear sizes of synthetic zeolites grains during water vapor adsorption. Proc. AS USSR, ser. Chem., 8: 1691-1697. (Ru)

Kozhuharov, M., S. N. Alyoshin, 1962. On the progress of separation of exchangeable bases and anions from some Bulgaria soils using electro-dialysis. Higher Agric. Inst. G. Dimitrov, Proc. Agronomy Faculty*, v.* 11, 105-122. (Bg)

Orr, C., J. M. Dalla Walle, 1959. Fine particle measurement, Macmillan, London, p.846.

Paterson, E., 1977. Specific Surface Area and Pore Structure of Allophonic Soil Clays. Clay Minerals, 12:1-9.

Rebinder, P. A., 1966. In: ”Physico-chemical mechanics of disperse structures”. Publ.”Nauka”, M., p. 400. (Ru)

Shull, C., P. Elkin, L. Roess, 1948. Physical Studies of Gel Microstructure. J. Am. Chem. Soc., 70:1410-1414.

Yets, D., 1964. In: “Catalysis. New physical methods and studies ”, Publ. “Mir”, M.: p.372. (Ru)

POROSITY OF THE SOIL ADSORBENT

Raytchev T.[1], Rousseva S.[1], Mehandjiev D.[2]
Hajnos M.[3], Jozefaciuk G.[3]

[1] N. Poushkarov Institute of Soil Science, 7 Shosse Bankja Str., 1080 P.O. Box 1369, Sofia, Bulgaria
[2] Institute of General and Inorganic Chemistry, Bulgarian Academy of Science, Sofia, Bulgaria
[3] Institute of Agrophysics, Polish Academy of Sciences, 4 Doswiadczalna Str., P.O. Box 201, 20-209 Lublin, Poland

Abstract

Theoretical analysis of the soil adsorbent's porosity is presented considering Eutric Vertisol and Eutric Planosol and based on low-temperature adsorption isotherms for nitrogen. It is established that their inherent structures are of transitionally-porous character. It is demonstrated how the dominating mineral type reflects on their structural-absorption characteristics. They reveal the porosity of the organo-mineral aggregates typical of the respective soil type and horizon, the differences between them and the modifications occurred along the soil profile depth.

It is indicated how the humus substances participate in developing the mesoporous structure, while integrating the individual mineral units in larger aggregative formations. Their removal or the system dispersion has a two-way action: from one side – opening of spaces available for the applied adsorptive, which diversifies the pore-size distribution, and from the other – reduction of micro-porous volumes inherent to these limited adsorbents.

Scheme is proposed to represent the possible impact of the applied treatments on the porosity, the organization of the organo-mineral structures and the morphology of the present clay minerals.

INTRODUCTION

The study of the state of the soil adsorbent, carried out on soils with diverse mineral composition and their clay fractions established dependence of the structural-adsorption characteristics on the amount and the dominating type clay minerals, humus content, and manner of binding in the organic-mineral associations. Its heterogeneous transitional porous structure reflects the dominating component in the composition of the primary organic-mineral matrix – the clay minerals. Their porous structure is composed of relatively larger flat parallel pores. The established presence of narrower pores is likely to be due to the availability of micro-voids between or in the walls of the lamellar pores. It can be assumed that this is a consequence of defects in the crystal structure of these minerals as well as of the influence of the organic modifier of the adsorption surfaces – the humic substances. Three fractions with diverse stability have been distinguished, which sensibility to the applied treatments depends on the strength of their binding in the organo-mineral association.

However, the representation of the adsorption isotherms in coordinates relative pressure – adsorbed amount makes difficult the reference of the studied objects to particular structural type. This is even more difficult for soils where simultaneous and dissimilar reaction of the individual components during adsorption impacts diversely the way of the obtained isotherms. In spite, it can be assumed that the porous adsorbent of the studied soils can be referred to the sorbents with expressed meso-porous character.

This assumption has been examined in this work testing the opportunity for diagnostics of the soil porosity by analysis on the regions of disposition of the isotherms represented in relative coordinates (Komarov, 1977).

MATERIAL AND METHODS

The study has been carried out on taken by the method of BET ((Brunauer et al., 1938)) low-temperature isotherms of nitrogen for soils and their clay fractions sampled from three horizons of Eutric Planosol (Velchevo village, Lovech district) and Eutric Vertisol (Sredetz village, Stara Zagora region).

Well expressed differentiation with respect to the profile distribution of the clay fraction characterizes the Eutric Planosol. The clay minerals in the surface horizon are represented mostly by aluminized chloride (21%), hydro-mica (16%) and kaolinite (16%) (Atanassov, 1977; Atanassov and Dimitrov, 1976). Montmorillonite dominate (37%) in the content of the clay minerals in the illuvial horizon, followed by hydro-mica (19%) and kaolinite (14%). There is similar distribution of the clay minerals and the other mineral components in the C horizon, but the montmorillonite content is even higher 44%.

The Eutric Vertisol has clayey texture without noticeable differences in the clay and the silt contents between the individual genetic horizons. The clay is the dominant texture fraction in this soil. The clay minerals of the montmorillonitic group dominate (~ 70%) in the composition of clay minerals, followed by illite (~ 14%) and kaolinite (~ 10%).

Clay fractions are extracted with any chemical treatment (Aydinyan, 1966).

The low-temperature adsorption-desorption isotherms taken from samples, pre-treated by hydrogen peroxide (Jackson, 1958), after applying electro-dialysis (Raytchev, 1996; Raytchev, 1997; Raytchev and Toncheva, 1997) and after combined treatment with hydrogen peroxide, sodium pyrophosphate and electro-dialysis.

The electro-dialysis is completed in a three-chamber apparatus with a capacity of each chamber of 0.250 l at constant values of the voltage (250 V) and the field gradient (50 V/cm), through cellophane membranes (Bolshakov, 1978; Kozhuharov and Alyoshin, 1962). The parameters have been controlled periodically by measuring the pH of the suspension in the middle chamber and that of the extracts in both outlying (Raytchev, 1996).

Obtained isotherms of the studied samples have been analyzed using their graphical representations in relative coordinates (Komarov, 1977). This enables their expression in a quadratic coordination system: the portion of the adsorbate in the phase of the adsorbent (θ) – relative vapour pressure.

RESULTS

According to Komarov (1977) the isotherm of the structure with ideal type is a straight line (AB), which divides diagonally the quadratic coordinate system, delineating regions corresponding to the main types of adsorbents: non-porous, micro-porous, meso-porous and macro-porous.

All isotherms located above this straight line are referred to fine-porous structure or at least structure enriched with micro-pores. Below it the isotherms of relative adsorption are laying, which testify to macro-porous structure. Isotherms of S-shape mode with a positive declination from the straight line AB in the region of the low values of the relative pressure (P/Po) and with a negative declination at high P/Po are inherent to adsorbents of meso-porous character. There are different cases possible in the zone of action of each of this isotherm types when the respective adsorbent structure is enriched with one or another type of pores. This is reflected by their proximity to 'the standard' straight line AB.

Figures 1 and 2 show differences in isotherms of clay fractions, extracted from the B horizons of both studied soils due to the treatments by hydrogen peroxide, sodium pyrophosphate and electro-dialysis. They are presented in a common manner (adsorbed amount vs. relative pressure) as well as in a quadratic coordinate system. In the first case, severe narrowing of the hysteresis is observed due to the increased aggressiveness of the combined treatment with hydrogen peroxide, sodium pyrophosphate and electro-dialysis. This is an indication of equalization of the pore type and their approximation to cylindrical form. There is no retention on the desorption branch; it decreases smoothly with the reduction of the relative pressure. This reflects the way of the isotherms in quadratic coordinates in reduction of the amount of micro-pores and increase in the diversity of the meso-pore sizes. The way of the curves becomes even steeper after electro-dialysis of samples pretreated by hydrogen peroxide and sodium pyrophosphate. The plot in quadratic coordinates reveals strong reduction in amount of micro-pores, which is less expressed for Eutric Vertisol. The micro-pores still dominate in the Vertisol while the Eutric Planosol reveals enrichment with larger pores.

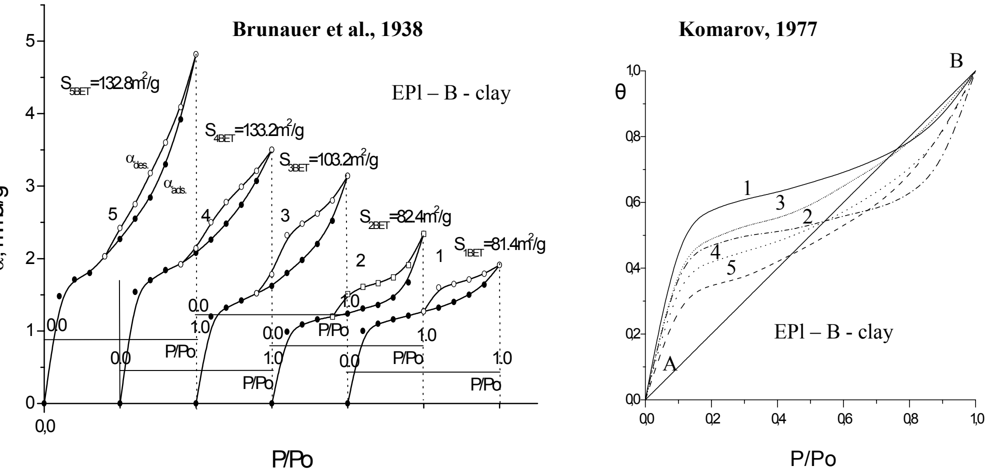


Fig. 1. Low-temperature nitrogen adsorption-desorption isotherms for < 2 µm clay fractions isolated from Eutric Planosol (EPl_{clay}), presented by BET (Brunauer et al., 1938) and in relative coordinate system (Komarov, 1977). α – adsorbed amount; 1 – untreated; 2 – treated with H_2O_2; 3 – electodialysed (ED); 4 - treated with H_2O_2 + $Na_4P_2O_7$; 5 - treated with H_2O_2 + $Na_4P_2O_7$ + ED. *each isotherm is shifted along the abscissa by P/Po = 0.5.*

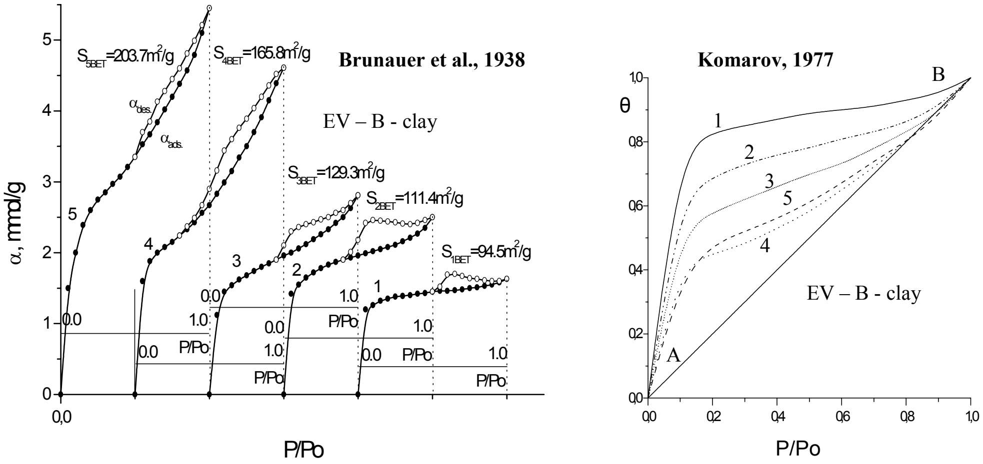


Fig. 2. Low-temperature nitrogen adsorption-desorption isotherms for < 2 µm clay fractions isolated from Eutric Vertisol (EV_{clay}), presented by BET (Brunauer et al., 1938) and in a relative coordinate system (Komarov, 1977). Notes as in Fig. 1.*

The isotherm of the initial soil sample from the A horizon of the Eutric Planosol in quadratic coordinates is strongly shifted towards the region of non-porous adsorbents. At the same time, the S-shape mode of the isotherm of its adsorbent has a positive declination from the straight line AB in the region of low values of P/Po and negative one – for higher relative pressure (fig. 3). This gives evidence for its mesoporous character, which reflects the dominating kaolinic type of its mineral composition with low porosity and small specific surface area. Their aggregation with the available humus creates the observed inhomogeneity in the sizes of the porous space. Their presence in dilute condition, such as the initial soil, mitigates the adsorption effect on the obtained isotherms, which reflect the extremely low porosity of the primary minerals in the studied soil.

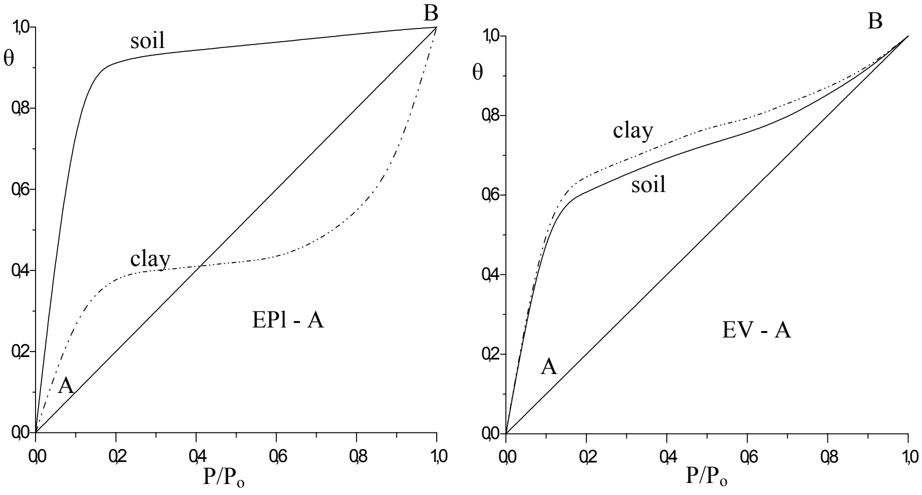


Fig. 3. *Low-temperature nitrogen adsorption isotherms in relative coordinates for soil (soil) and < 2 µm clay fractions (clay) isolated from A horizons of Eutric Planosol (EPl) – v. Velchevo (EPl – A) and Eutric Vertisol (EV) – v. Sredetz (EV – A)*

The change of the dominating mineral type in the soil from kaolinic to montmorillonitic shifts the isotherms above the line AB at low relative pressures and approaches this line in the region of high ones (figs 1, 2, 3). The enrichment with finer pores is reflected in the isotherm of the initial sample, as a consequence of high clay content (about 50 %). This is stronger reflected in the isotherms of the Eutric Vertisol, where the positive declination from the line AB at high values of P/Po is higher (figs 1, 2, 3). This effect is in conformity with the expressed montmorillonitic character of the clay minerals in Eutric Vertisol being much higher than in Eutric Planosol.

Partial removal of organic matter from initial sample rich in kaolin type minerals opens certain porous space that is seen from the isotherm close to the line AB in the region of the low values of P/Po (fig. 1). It can be assumed that the removal of the humus components bonded with the lateral surfaces of the clay minerals for the conditions of the studied soil opens between-package spaces, which become available for the applied adsorbtive. The dispersion of the organic-mineral particles after electro-dialysis has similar but more strongly expressed effect.

The effect of the applied treatments on the position of the adsorption curves in the considered regions is not so well expressed when the clay fraction of the Eutric Planosol becomes more enriched with montmorillonitic minerals and its amount increases. This is confirmed by the position of the isotherms of the initial samples of the Eutric Vertisol as well as by the isotherms of the extracted organo-mineral colloids.

It can be assumed that the treatment by hydrogen peroxide and the single application of electro-dialysis in the indicated regime of functioning do not influence the morphology of the existing clay minerals. However, in both cases there is disaggregation and opening of additional volume in the structure of the soil adsorbent (fig. 4).

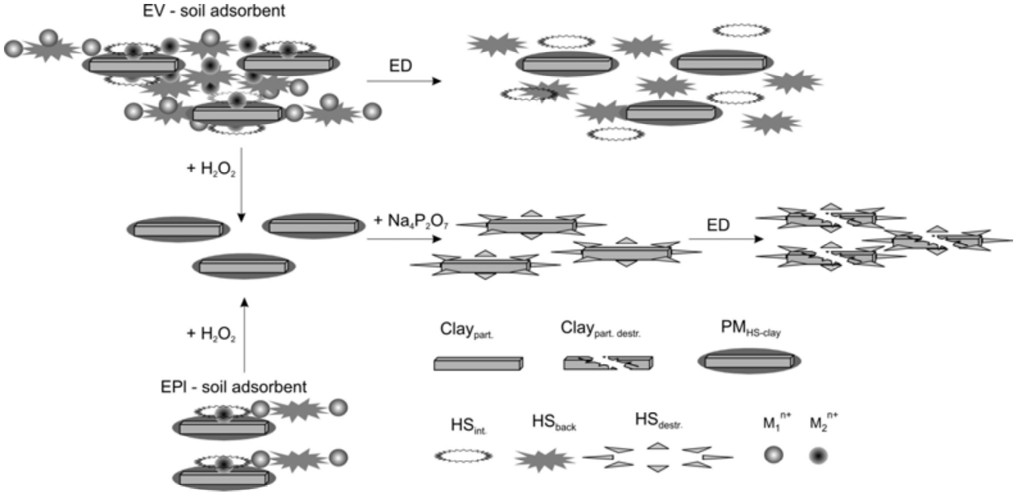


Fig. 4. *Modifications in the structure of the soil adsorbent (SA) of Eutric Vertisol (EV) and Eutric Planosol (EPl) after treatment by H_2O_2, $Na_4P_2O_7$ and electrodialylisis (ED).*
$PM_{HS\text{-}clay}$ – primary organo-mineral matrix of SA; $HS_{int.}$ – humus substance from the internal layer of soil adsorbent; HS_{back} - humus substance from external layer of SA; $HS_{destr.}$ - humus substance in primary organo-mineral matrix of SA after destruction; $Clay_{part.}$ – Clay particle; $Clay_{part.destr.}$ – Clay particle after destruction; M_1^{n+} - exchangeable cations; M_1^{n+} - cation-bridges between organic and organo-mineral layers.

It is mostly on account of pores with larger sizes while this effect is more strongly expressed at the Eutric Vertisol. This is likely to be related to the higher degree of aggregation of the individual organic-mineral units, which is a consequence of the high content of calcium ions in the reaction media. The base saturation is rather low at the Eutric Planosol and the additional disaggregation does not impact seriously the adsorbent's porosity. Additional treatment by sodium pyrophosphate affects also a part of the organic matter, which is strongly bonded with the mineral kernel forming the primary organic-mineral matrix ($PM_{HS\text{-}clay}$). Newly opened mineral surfaces reduce the stability of the crystal lattice towards the applied regime of electro-dialysis (fig. 4) while impacting the morphology of the existing clay minerals.

CONCLUSIONS

The results from the accomplished analysis of the isotherms of the studied soils samples prove the assumptions for the transitionally porous character of the soil adsorbent's structure. The dominant mineral type affects their structural-adsorption characteristics, which reflect the porosity of the organic-mineral aggregates inherent to the soil type and horizon, the differences between them and the modifications occurred along the soil profile depth. The differences in the mode of the isotherms of the individual genetic horizons of the Eutric Planosol are related to the diverse texture of the samples taken from different profile depths. The humus substances contribute actively in the development of the meso-porous structure, while unifying the individual mineral units in larger aggregative formations. Their removal or the dispersion of the system act in two ways: on the one hand – newly opened spaces become available for the applied adsorptive, which diversifies the pore-size distribution, while on the other hand – it is established reduction of the micro-porous volumes, which are inherent to these organic adsorbents.

REFERENCES

Atanassov, Iv., 1977. Weathering and evolution of mineral part of the soils in Bulgaria. D. Sci. Thesis, Higher Agric. Inst., Sofia, p.566. (Bg)

Atanassov, Iv., D. N. Dimitrov, 1976. Distribution of the fine-dispersive minerals within the profile of light-grey gleyic soils. Soil Science and Agrochemistry, (XI) 3:17-25. (Bg)

Aydinyan, R. H., 1966. Accelerated method for extraction of soil clay and colloids using super-centrifuge. Agrochemistry, 6:151-156. (Ru)

Bolshakov, V., 1978. Application of the method of electro-dialysis for soil studies. Proc. Soil Sci. Inst. Dokuchaev W.W., M. (Ru)

Jackson, M. L., 1958. Soil Chemical analysis, New York:Prentice-Hall, p.498.

Komarov, V. S, 1977. Adsorbents and their properties, Publ. "Nauka i Tehnika"Minsk. 248 p. (Ru)

Kozhuharov, M., S. N. Alyoshin, 1962. On the progress of separation of exchangeable bases and anions from some Bulgaria soils using electro-dialysis. Higher Agric. Inst. G. Dimitrov, Proc. Agronomy Faculty*, v.* 11, 105-122. (Bg)

Raytchev, T., 1996. Influence of organo-mineral interactions on colloid-chemical state of the soil adsorbent. D. Sci. Thesis, "N. Poushkarov" Inst., Sofia, 161 pp. (Bg).

Raytchev, T., 1997. Kinetics of the desorption of cations. II. Desorption of exchangeable calcium depending on humus quality in the soil, Soil science, Agrochemistry and Ecology, Sofia, vol. XXXII, 4:37-39. (Bg).

Raytchev, T., R. Toncheva, 1997. Kinetics of the desorption of cations. I. A mathematical model testing, Soil science, Agrochemistry and Ecology, Sofia, vol. XXXII, 4:34-36. (Bg).

IMPACT OF THE ANALYTICAL TREATMENTS ON THE CRYSTALO-CHEMICAL CHARACTERISTICS OF THE MINERAL PART OF THE SOIL ADSORBENT

Raytchev T.[1], Donov D.[1], Paskaleva K.[1], Hubenov G.[1]
Sokolowska Z.[2], Jozefaciuk G.[2],

[1] N. Poushkarov Institute of Soil Science, 7 Shosse Bankja Str., 1080 P.O. Box 1369, Sofia, Bulgaria
[2] Institute of Agrophysics, Polish Academy of Sciences, 4 Doswiadczalna Str., P.O. Box 201, 20-209 Lublin, Poland

Abstract

Clay fractions extracted by the method of Aydinyan (1966) have been studied to determine the impact of their treatment with H_2O_2, $Na_4P_2O_7$+H_2O_2 and $Na_4P_2O_7$+H_2O_2, and electro dialysis on the crystalo-chemical and structure-adsorption status of the soil adsorbent of Planosol and Vertisol. Results from roentgen-structural, differential-thermic and electron-microscopic analyses have demonstrated convincible that treatment with H_2O_2 and electro-dialysis do not change the crystal lattice of clay minerals but slightly increase their dispersibility. Treatment with $Na_4P_2O_7$ for removing organic matter is not justifiable against their further physico-chemical characterization, as it results in partial destruction of their crystal construction and structure. Simultaneous application of electro-osmosis and ultra-filtration has enabled development of method for extraction of soil colloids by electro-ultra-filtration. Opportunity has been arisen for a significant acceleration of the extraction as compared to the traditionally applied analytical methods, avoiding the necessity of chemical pre-treatment, which is an important precondition for conducting mineralogical analyses. Analysis of the obtained preparations for physico-chemical and mineralogical analyses has not shown destructive impacts on the clay minerals. The simplified construction enables usage of the method in each laboratory conducting similar studies.

INTRODUCTION

Mechanisms of interaction between mineral and organic soil colloids are of definitive practical interest as they are related to sorption properties and acid-alkaline balance in the soil adsorbent. Availability of nutrients for plants depends on the velocity of their transition from the solid to the liquid soil phase. Humus substances themselves influence the ion-exchange properties of clay minerals with diverse nature in a different manner. However, the type of exchangeable ions has also an important role for forming organic-mineral associates and developing their colloid-chemical structure. In most cases their mobility in the micelle volumes is lower than the functioning of the root system. In some cases clarification of these interactions requires removal of some components of the system by means of suitable treatments. This work follows up the influence of different treatments used for removal of organic matter and exchangeable cat ions on eventual modifications in the mineral structure of the studied objects.

MATERIALS AND METHODS

Clay fractions, isolated using the method of Aydinyan (1966) from B-horizons of Eutric Planosol (Velchevo village, Lovech district – horizon B_2 62 – 82 cm) and Eutric Vertisol (Sredets village, Stara Zagora district – horizon B_1 62 – 90 cm) were used. Both soils are located in the transitional-continental sub zone (Subev, 1960).

The texture of the soil sample from illuvial horizon of the Eutric Planosol is clayey. The composition of the clay minerals is characterized by domination of the montmorillonite (37%), followed by hydro-mica (19%) and kaolinite (14%). The amount of the fine-dispersive quartz (13%) decreases markedly compared to the surface horizon, while the non-silicate compounds of Si, Al and Fe tend to increase slightly (7%) (Atanassov, 1977; Atanassov and Dimitrov, 1976). The clay fraction has been extracted from a soil sample with characteristics as follows: pH_{H2O} – 5.7; %C – 0.93; particles < 0.001 mm – 54%; particles < 0.01 mm – 61.9%. The following soil physico-chemical characteristics have been determined following the method of Ganev and Arsova (1980): $T_{8.2}$ = 19.32 cmol.kg^{-1}; T_{CA} = 15.40 cmol.kg^{-1}; T_A = 3.92 cmol.kg^{-1}. The specific surface area, determined by low-temperature adsorption of nitrogen and calculated according to the BET method (Brunauer et al., 1938) is S_{BET} = 54.4 m^2/g.

The texture of the soil sample from the studied Eutric Vertisol is also clayey with domination of the clay fraction in the particle-size distribution. There is no significant heterogeneity in the distribution of clay minerals within the soil profile depth. The composition of the clay minerals is described by domination of the montmorillonitic group (71%), followed by illite (14.2%) and kaolinite (9.8%). Certain amount of hydro-goethite (4.9%) is found as well (Atanassov, 1977). The clay fraction has been extracted from a soil sample with the following characteristics: pH_{H2O} – 7.90; %C – 1.22; particles < 0.001 mm – 52.4%; particles < 0.01 mm – 73.5%; $T_{8.2}$ = 33.10 cmol.kg^{-1}; T_{CA} = 30.7 cmol.kg^{-1}; T_A = 2.60 cmol.kg^{-1}; S_{BET} = 76.6 m^2/g.

The clay fraction extracted from the Eutric Planosol has physico-chemical characteristics, determined after Ganev and Arsova (1980) as follows: $T_{8.2}$ = 31.30 cmol.kg^{-1}; T_{CA} = 22.40 cmol.kg^{-1}; T_A = 10.3 cmol.kg^{-1}. The specific surface area determined by low-temperature adsorption of nitrogen and calculated according to the method of BET (Brunauer et al., 1938) is S_{BET} = 81,4 m^2/g. The content of C is 1.34 %.

The clay fraction extracted from the Eutric Vertisol has physico-chemical characteristics, determined after Ganev and Arsova (1980) as follows: $T_{8.2}$ =44.4 cmol.kg^{-1}; T_{CA} = 36.9 cmol.kg^{-1}; T_A = 3.5 cmol.kg^{-1}. The specific surface area determined by low-temperature adsorption of nitrogen and calculated according to the method of BET (Brunauer et al., 1938) is S_{BET} = 94.5 m^2/g. The content of C is 1.75 %.
2. Clay fractions separated by the method of Aydinyan (1966) and by electro-ultra-filtration (Raytchev et al., 1983) from soils (A, B and C), sampled from three acid soils (light grey -A, grey -B and dark grey -C). All three soil samples are no calcareous with pH_{H2O} 5 ÷ 6.5. Comparisons are based on data from electron-microscopic and roentgen-structural analysis keeping instrumental conditions as described below.

The samples from extracted clay fractions have been treated as follows:

- Treatment with hydrogen peroxide with heating on water bath (Jackson, 1956);
- Treatment with hydrogen peroxide and 0.1M $Na_4P_2O_7$ at the same conditions;
- Electrodialysis of initial and H_2O_2 and 0.1M $Na_4P_2O_7$ pretreated samples (Raytchev, 1997; Raytchev and Toncheva, 1997);

The electro-dialysis has been accomplished in three-chamber apparatus with a capacity of each chamber of 0.250 l at constant values of the voltage (250 V), field gradient (50 V/cm) through cellophane membranes (Raytchev, 1996). The extraction has been accomplished very carefully, in view of the susceptibility of the clay minerals to disintegrate easily at increased current densities. Above conditions have been controlled by periodical measuring pH of the suspension in the middle chamber and the extracts in both outlying chambers.

The humus content has been determined by modified method of Turin by means of oxidation by bichromate /H_2SO_4 at 120^{o}C for a period of 45 min and catalyst Ag_2SO_4, and reverse titration with $(NH_4)_2SO_4.FeSO_4.6H_2O$ (Kononova, 1966).

The modifications in the structure of the crystal lattice of the minerals occurred as a result of the applied treatments have been controlled by means of structure-adsorption, differential-thermic, roentgen-structural and electron-microscopic analyses.

The specific surface area (S_{BET}) of the initial samples and these treated by the indicated manners has been determined via the BET method using data from low temperature adsorption of nitrogen vapours (Brunauer et al., 1938).

The surface of the meso-pores (S_p) and the volume of micro-pores (V_μ) have been calculated on the basis of the adsorption data for the adsorption value at the beginning of the hysteresis (α_i, mmol/g) and the maximal adsorbed amount (α_{max}) at P/P_0 = 1.0 (Kiselev, 1949; Dubinin, 1966; 1970). The volume of meso-pores (V_p) has been determined as a difference between the total volume of the sorption space (V_0) and the volume of micro-pores: $V_p = V_0 - V_\mu$.

The interpretation of the output data is based on the classification of Dubinin (1970; 1972), which distinguishes the pores according to their effective radius between micro- (< 2 nm), transitional or meso-pores (2÷20 nm) and macro-pores (>20 nm).

The DTA was performed using the apparatus of Paulic and Erdey for heating velocity – 10° per min; sample mass – 0.5 g; heating interval – 20°÷1000°C; galvanometer sensibility: DTA – 1/10, TG – 200 mg for the entire scale.

The EM studies have been completed using electron microscope UEMV-100B for spot targets at voltage of 75 kV and total magnification of 27 000 times.

The XRD structural analysis has been completed by means of diffractometer DRON 1 at voltage of 39 kV, amperage of 9 mA using monochromatic radiation Co-K_α at spinning velocity of 2° per min.

RESULTS

Clay fractions separated by the method of Aydinyan (1966)

After partial removing the organic matter by hydrogen peroxide (tab. 1) S_{BET} of the samples extracted from Eutric Planosol is not changed while the surface area of the transitional pores (S_p) is reduced (tab. 1). Indication of similar redistribution is also the fact that the total pore volume (V_o) decreases slightly on account of the meso-pores (V_p), while the volume of micro-pores (V_μ) increases.

Table. 1. Physico-chemical characteristic of clay fractions (particle < 2μm), extracted from Eutric Planosol (EP) and Eutric Vertisol (EV)

Site / Sample No.		Bound H_2O		Constitutional H_2O		S_{BET}, m^2/g	S_p, m^2/g	Pore volume, $(cm^3/g)x10^2$			C, %
		T^{max}, °C	WL, %	T^{max}, °C	WL, %			Vo	Vp	Vμ	
EP	1	142	12.0	540	8.2	81.4	37.0	8.2	5.4	2.8	1.34
	2	140	11.6	530	8.0	82.4	24.0	6.6	3.1	3.5	0.59
	3	138	12.4	530	7.6	103.2	73.0	10.8	8.4	2.4	1.57
	4	158	16.4	540	5.2	133.2	86.0	12.1	8.6	3.5	0.24
	5	160	17.0	530	5.0	132.8					0.35
EV	1	150	17.2	550	7.2	94.5	10.0	5.5	0.7	4.8	1.75
	2	150	16.4	540	7.0	111.4	26.0	8.5	3.0	5.5	0.53
	3	140	17.8	540	6.2	129.3	49.0	9.7	5.0	4.7	1.94
	4	160	18.4	520	4.8	165.8	141.0	16.3	13.2	3.1	0.19
	5	140	14.8	520	4.2	203.7	91.4	18.8	10.4	8.4	0.20

1 – initial sample; 2 – after treatment with H_2O_2; 3 – after electro-dialysis; 4 – after treatment with $Na_4P_2O_7$ + H_2O_2; 5 – after treatment with $Na_4P_2O_7$ + H_2O_2 +electro-dialysis; S_{BET} – specific surface area, determined from low-temperature adsorption of nitrogen vapours (Brunauer et al., 1938); S_p – surface area of the transitional pores, calculated after Kiselev (1949); V_μ – volume of micro-pores; V_o – maximal pore volume; V_p – volume of the transitional pores.

Removal of the organic matter by hydrogen peroxide for the sample, extracted from Eutric Vertisol, increases S_{BET} and the surface area of meso-pores (S_p) (tab.1). The total pore volume (V_o) is also on increase and it is on account of the meso-pores volume (V_p).

After electro-dialysis of the studied samples, both the specific surface area and the total pore volume increase sharply, while the volume of micro-pores remains almost the same (tab.1). Latest means that after electro-dialysis the meso-pores are the main bearer of the surface area. This treatment results in disaggregation and probably dispersion of the available clay particles on account of the extracted cat ions and disintegrated linkages with humic substances.

After removing the organic matter by $Na_4P_2O_7$+H_2O_2 (Fig.1) the distance between the adsorption and the desorption branch of the isotherms decreases.

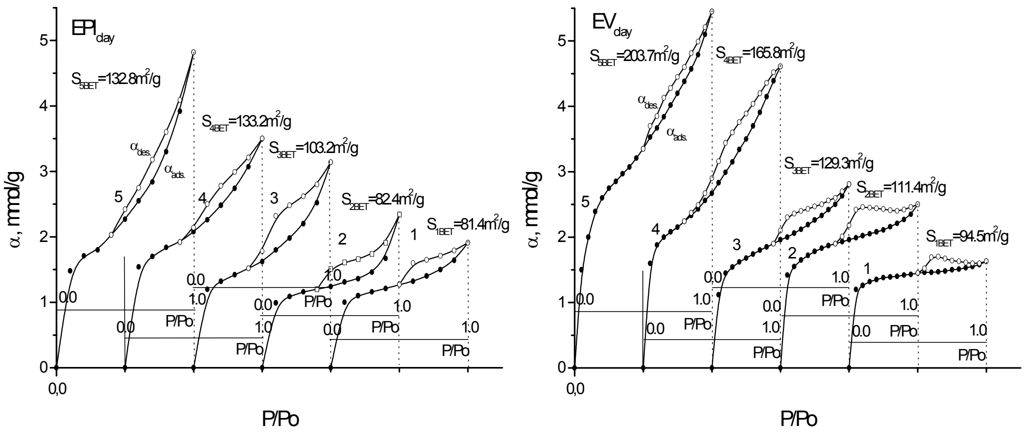


Fig. 1. *Low-temperature nitrogen adsorption-desorption isotherms for < 2 μm clay fractions isolated from Eutric Planosol (EPl_{clay}) and Eutric Vertisol (EV_{clay}) (each isotherm is shifted along the abscissa by P/Po = 0.5). α – adsorbed amount; 1 – untreated; 2 – treated with H_2O_2; 3 – electodialysed (ED); 4 - treated with H_2O_2 + $Na_4P_2O_7$; 5 - H_2O_2 + $Na_4P_2O_7$ + ED.*

This is an indication for equalization of the pore kind and their approximation to cylindrical form (Komarov, 1977). There is no retention in the desorption curves and they decrease smoothly with decreasing the relative pressure, which is possible only for pores withal kinds of sizes. This is proved also by the strong scattering around their mean radius (Fig.2). The surface area of the meso-pores increases strongly and approaches the values determined after electro-dialysis for the same samples. After this treatment the total pore volume (V_o) increases most strongly and it is on account mostly of the meso-pores volume (V_p) (tab.1).

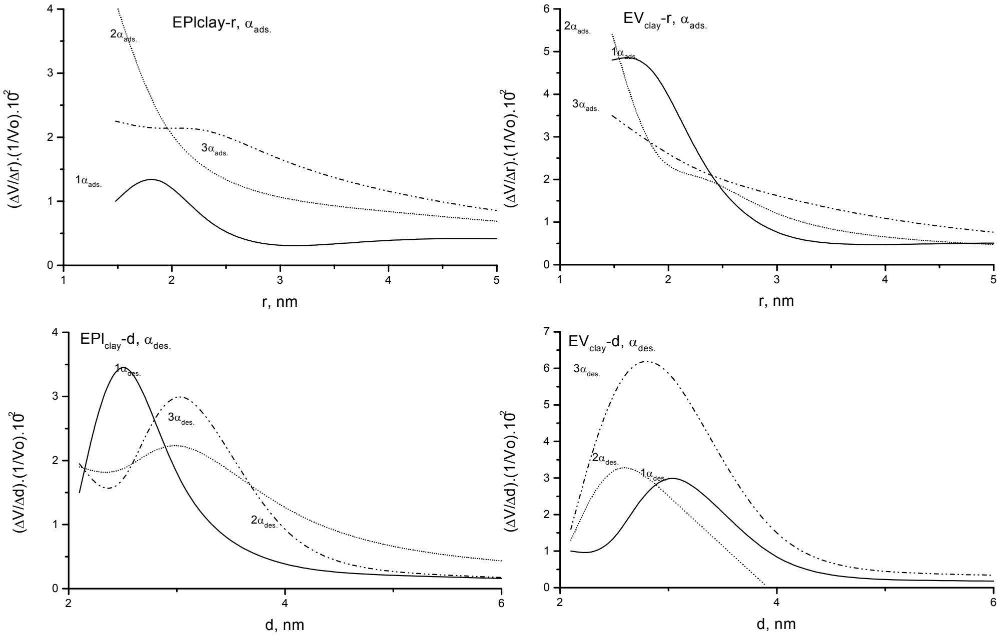


Fig. 2. *Pore-size distribution for < 2 μm clay fractions isolated from Eutric Planosol (EPl_{clay}) and Eutric Vertisol (EV_{clay}) calculated by the method of Orr and Dalla Walle (r, $\alpha_{ads.}$); by the method of Innes (d, $\alpha_{des.}$). 1 – untreated; 2 – treated with H_2O_2; 3 – electodialysed; ΔV – volume of the filled pores corresponding to Δr; Vo – total pore volume.*

After electro-dialysis of the samples pre-treated by this mean, the curves become the more so as steeper. The hysteresis decreases and the specific surface area increases strongly. All these are indication for occurring extremely severe changes in the morphology of the studied subjects.

The data from diffractometric analyses (Fig.3) show that montmorillonitic, hydro-mica and kaolinic minerals are presented in the studied initial samples for both soils. From quantitative viewpoint, the content of minerals from the montmorillonitic group is the highest.

There are no modifications in the structure of the crystal lattice of the clay minerals after partial removal of the organic matter by hydrogen peroxide. Just the contrary, a point to note is the slight increase of the intensity of reflections of 001, especially that of the montmorillonite, conditioned by the better organization of the clay minerals in axis C.

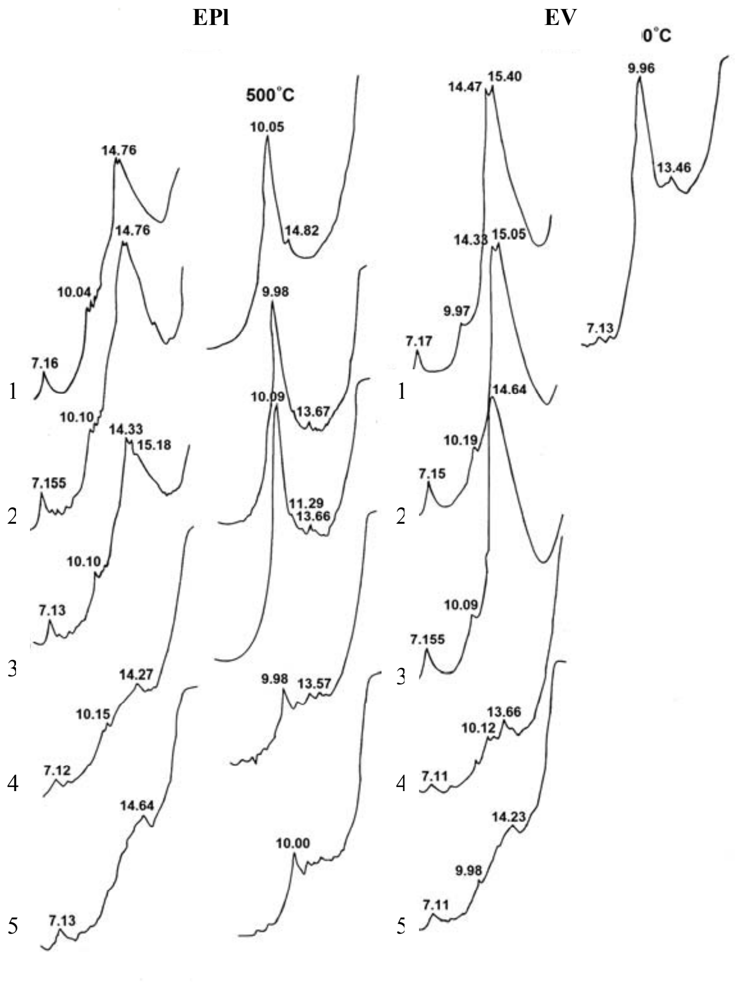


__Fig. 3.__ Diffractograms of clay fractions extracted from B-horizons of Eutric Planosol (EPl) and Eutric Vertisol (EV)

1 – initial sample; 2 – after treatment by H_2O_2; 3 – after electro-dialysis; 4 – after treatment by $Na_4P_2O_7$+H_2O_2; 5 – after treatment by $Na_4P_2O_7$+H_2O_2+electro-dialysis.

Sample treatment by electro-dialysis has no particular effect on the structure of the crystal lattice of the clay minerals, but the sample from the Eutric Planosol shows noticeable dispersibility of the montmorillonitic minerals.

Significant modifications in the diffractograms occur after treatment of the clay fraction with c $Na_4P_2O_7+H_2O_2$. This shows that this treatment affect very sensibly the structure of the crystal lattice of the clay minerals expressed in its disintegration and amorphization. The disintegration is not complete (Fig.3) but it affects significant part of the clay minerals –about 70% - 80%. Most deeply affected are the minerals from the montmorillonitic group. There is similar picture of the samples treated by $Na_4P_2O_7+H_2O_2$ and followed up electro-dialysis, though the degree of disintegration is less pronounced.

The data from the thermic analysis support completely the conclusions drawn on the basis of the diffractometric studies. The thermograms from DTA (Fig.4) show certain increase of the areas from the endothermic effects at 138^o – 160^oC, characterizing the extraction of adsorbed water from the clay minerals and the available amorphous phases.

The size of the endothermic maximums at 520^o – 550^oC decreases in direction: initial sample = treated by H_2O_2 > after electro-dialysis > treated by $Na_4P_2O_7+H_2O_2$ > treated by $Na_4P_2O_7+H_2O_2$ and followed up electro-dialysis. The examined endothermic effect is a result of extraction of constitutional water from the minerals 2:1 and 2:2 and disintegration of the structure of the crystal lattice of the minerals of 1:1 type.

Exothermic effects are observed at the endmost region of development of DTA with a maximum at 895^o – 900^oC for the samples from Eutric Planosol and at 880^o – 920^oC – for the samples from Eutric Vertisol. Such an effect is absent after treatment with $Na_4P_2O_7+H_2O_2$ and after electro-dialyzing of the samples treated by this manner. This absence is related to the complete disintegration of the structure of the crystal lattice of the clay minerals.

There is an exothermic effect also at the low-temperature region with a maximum at 330^o – 360^oC for the samples from Eutric Planosol and at 320^o – 390^oC – for the Eutric Vertisol. The size of the maximum decreases in direction: initial sample = electro-dialysed sample > treated by H_2O_2 > treated by $Na_4P_2O_7+H_2O_2$ > treated by $Na_4P_2O_7+H_2O_2$ and followed up electro-dialysis. This exothermic effect is related to thermic destruction of the organic matter and its decrease following certain treatment is a consequence of the partial or full removal of the humic substances.

Losses of weight have been calculated from the TG-curves, not presented in Fig. 4. The data for the water bounded by adsorption are presented in tab.1. It should be noticed that the effect, expressed by the first endothermic maximum, increases with the raise of dispersibility and the amount of amorphous substances. The content of hygroscopic water increases after treatment with $Na_4P_2O_7+H_2O_2$ and after electro-dialysis of samples pre-treated by this manner, which can be related to the increased dispersibility and amorphisation of the mineral phases.

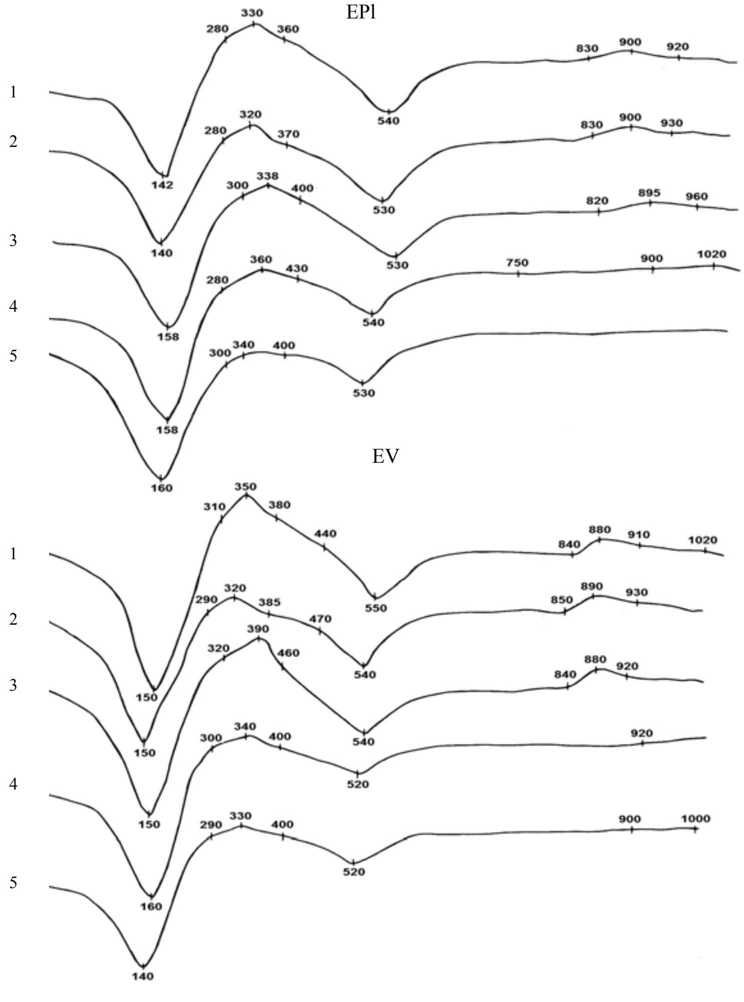
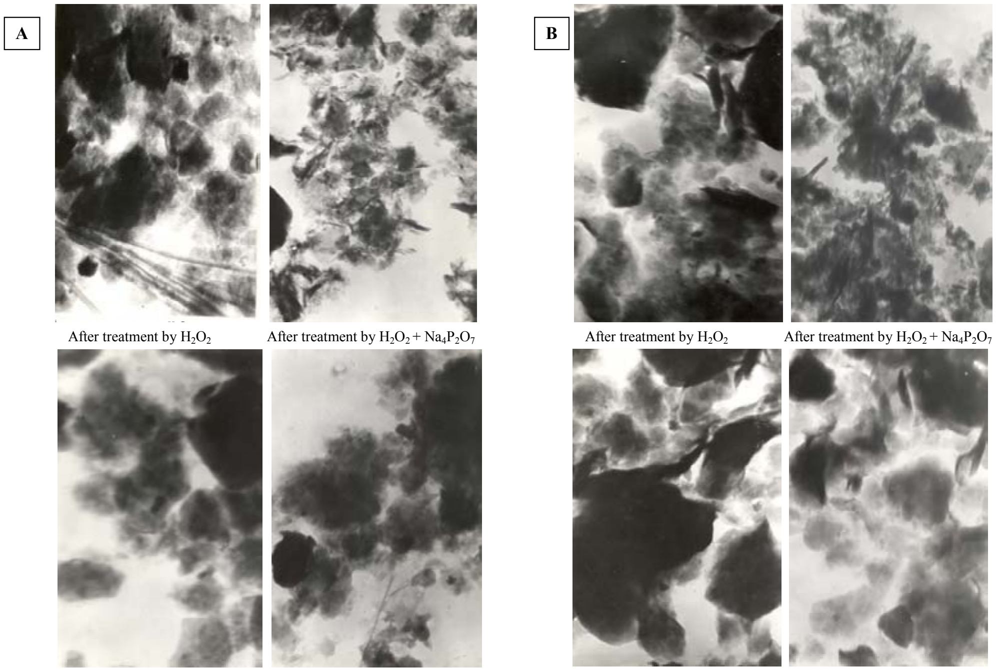


__Fig. 4.__ Derivatograms of clay fractions extracted from B-horizons of Eutric Planosol (EPl) and Eutric Vertisol (EV)
1 – initial sample; 2 – after treatment by H_2O_2; 3 – after electro-dialysis; 4 – after treatment by $Na_4P_2O_7$+H_2O_2; 5 – after treatment by $Na_4P_2O_7$+H_2O_2+electro-dialysis

The content of constitutional water decreases for the samples of both soils in direction: initial sample = treated by H_2O_2 > treated by $Na_4P_2O_7$+H_2O_2 > treated by $Na_4P_2O_7$+H_2O_2 and followed up electro-dialysis. The percentage content of constitutional water does not change after treatment with hydrogen peroxide. In this case, the crystal lattice of the fine-dispersive minerals composing the clay fraction is not affected. The strongly decreased content on constitutional water in the samples after their treatment with $Na_4P_2O_7$+H_2O_2 and $Na_4P_2O_7$+H_2O_2 and electro-dialysis unequivocally demonstrates the disintegrating affect of these treatments on the structure of the crystal lattice of the clay minerals.

This is confirmed also by the electron-microscopic studies. After sample treatment with H_2O_2, the degree of dispersibility is better, the minerals are with clearly pronounced boundaries while the minerals and the kaolinite and the mica are still better expressed, while the minerals with blurred boundaries are no affected and their morphology is complete (Fig.5).



After treatment by H_2O_2 After treatment by H_2O_2 + $Na_4P_2O_7$

Initial sample After electrodialysis

After treatment by H_2O_2 After treatment by H_2O_2 + $Na_4P_2O_7$

Initial sample After electrodialysis

Fig. 5. *Electron-microscopic photographs of clay fraction from B horizons of Eutric Planosol (A) and Eutric Vertisol (B)*

This is logical, since the organic matter binds together the clay minerals and after its removal the crystal morphology becomes clearer in the microscope. The observations show that the electro-dialysis strengthens also the degree of dispersibility without affecting significantly the crystal lattice of the clay minerals. However, the treatment of the clay fraction with $Na_4P_2O_7$+H_2O_2, regardless of its accompaniment with electro-dialysis, results in radical changes in the morphology of all clay minerals and especially these with blurred boundaries, such as the montmorillonite and the mixed-layered minerals. All the crystals in the so treated samples are with disturbed morphology, severely torn to amorphyzed. New crystals with elongated form similar to the iron hydroxides are obtained in some cases. Traces from in disintegrated minerals – probably mica and hydro-mica, are observed at separate locations in the samples.

Clay fractions, extracted by electro-ultra-filtration

Extraction of the clay fraction from soil is indispensable condition for conducting physico-chemical end mineralogical studies. Existing current methods for separating clay minerals are very slow, labour-consuming and need preliminary mechanical or chemical dispersion. The presence of electrical charges on the surface of the soil colloids determines their sensibility to electro-chemical impacts. This is in the basis of a method developed for their accelerated extraction by combining the processes electro-osmosis and ultra-filtration (Raytchev et al., 1983). It is established that the electro-osmosis favours disaggregating of clay particles and their discharge on the ceramic membranes while the ultra-filtration accelerates their movement in the electric field and at the same time contributes to avoidance of the drastic acidification of the media. Based on methodological studies a device has been proposed (Fig.6) to realize the method, as well as the respective progress and regime of work (Raytchev et al., 1983):

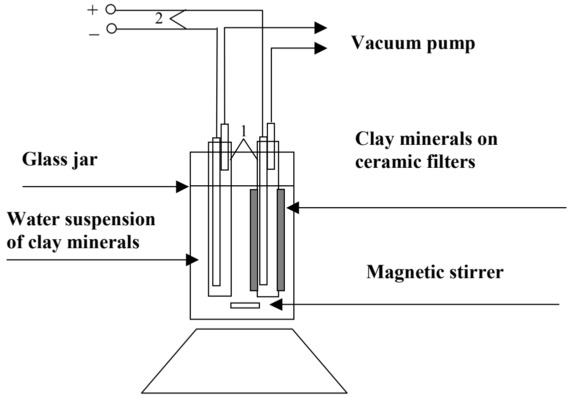


Fig. 6. *Device for separation of clay minerals through electroosmosis and ultrafiltration (Raytchev et al., 1983) (1 – ceramic filters; 2 – metal electrodes).*

Certain amount of soil sieved through a mash sieve with openings φ 1 mm is placed in a suitable glass container, poured with distilled water and stirred up with a magnetic stirrer. Ceramic bacterial membranes with chrome-nickel electrodes connected with a stabilized rectifier are sunk in the suspension and a water pump is plugged in by way of safety bottles. The voltage and the distance between the electrodes is regulate to such an extent that the field gradient is within the limits of 80 V/cm. Distilled water is added during the extraction. The material detached on the positively charged membrane is collected in a separate container. The process duration is in the limits of 3-4 hours and depends on the colloid part of the soil sample.

Comparative diffractometric studies accomplished with clay fractions, extracted by the method of Aydinyan and by means of electro-ultra-filtration show content of the same mineral phases (Raytchev and Donov, 1983). There is no considerable difference with respect to the quantity nor yet to modifications in the crystalo-chemical condition of the clay minerals in the studied samples.

CONCLUSIONS

Comparisons of the results from the applied methods for studying the crystalo-chemical and the structure-adsorption condition of the soil adsorbent after different treatments of the samples show that treatment with H_2O_2 and electro-dialysis accomplished in accordance with the noted conditions do not change the structure of the crystal lattice of the clay minerals but slightly increases their dispersibility.

Treatment with $Na_4P_2O_7$ for removing the organic matter from the clay minerals cannot be justifiable with a view to their further physico-chemical characterization as far as it results to partial disintegration of their crystal structure and lattice.

The method proposed for extraction of soil colloids by electro-ultra-filtration accelerates significantly the obtaining of preparations for physico-chemical and mineralogical analyses and does not have destructive impacts on the inherent clay minerals (Atanassova et al., 2004). The simplified construction enables the usage of the method in each laboratory, carrying similar studies.

REFERENCES

Atanassov, Iv., 1977. Weathering and evolution of mineral part of the soils in Bulgaria. D. Sci. Thesis, Higher Agric. Inst., Sofia, p.566. (Bg)

Atanassov, Iv., D. N. Dimitrov, 1976. Distribution of the fine-dispersive minerals within the profile of light-grey gleyic soils. Soil Science and Agrochemistry, (XI) 3:17-25. (Bg)

Atanassova, I., M. Benkova, T. Raytchev, G. Józefaciuk, 2004. Analysis of a technogenically degraded soil using a rapid method for clay fraction separation. In: “Modern physical and physicochemical methods and their applications in agroecological research”. Andrzej Bieganowski, Grzegorz Józefaciuk, Ryszard

Walczak (Ed), Centre of Excellence for Applied Physics in Sustainable Agriculture AGROPHYSICS, Nikola Poushkarov Institute of Soil Science, Institute of Agrophysics Polish Academy of Sciences, Lublin – Sofia 2004, pp. 7-10.

Aydinyan, R. H., 1966. Accelerated method for extraction of soil clay and colloids using super-centrifuge. Agrochemistry, 6:151-156. (Ru)

Brunauer, S., P. H. Emmet, E. Teller, 1938. Adsorption of gases in multimolecular layers. Journal of American Chemical Society, 60, 309 – 314.

Ganev, S., A. Arsova, 1980. Methods for determination of the strongly acidic and weakly acidic cation exchange in soils. Sofia, Soil Sci. and Agrochemistry,15 (3): 22-33 (Bg).

Jackson, M. L., 1956. Soil Chemical analysis – Advance course: Published by the author, Univ. of Wisconsin, Madison, Wis

Kiselev, A. V., 1949.Coll.”Problems of kinetics and catalysis”, M.-L., 6, 171. (Ru)

Kononova, M. M., 1966. Soil organic matter. It's nature, it's role in soil Formation and Soil Fertility. 2nd English Ed., Pergamon Press Inc., Elmsformd M.V., 544 pp.

Raytchev, T., 1997. Kinetics of the desorption of cations. II. Desorption of exchangeable calcium depending on humus quality in the soil, Soil science, Agrochemistry and Ecology, Sofia, vol. XXXII, 4:37-39. (Bg).

Raytchev, T., D. Donov, 1983. A rapid method for Extracting the clay fraction from soil, Soil Science and Agrochemistry, Sofia, vol. XVIII, 5:88-93. (Bg).

Raytchev, T., R. Toncheva, 1997. Kinetics of the desorption of cations. I. A mathematical model testing, Soil science, Agrochemistry and Ecology, Sofia, vol. XXXII, 4:34-36. (Bg).

Raytchev, T., 1996. Influence of organo-mineral interactions on colloid-chemical state of the soil adsorbent. D. Sci. Thesis, “N. Poushkarov” Inst., Sofia, 161 pp. (Bg).

Raytchev, T., V. Zhelev, D. Donov, B. Zografov, 1983. Method for extraction of the soil colloid fraction and separating the primary minerals for mineralogy analysis. Reg. N^o 56074/02.04.1982, Bull. N^o 5/16.05.1983, Auth. Certif. N^o 33774/07.09.1983, Sofia, Bulgaria. (Bg)

HUMUS SYSTEM STABILITY OF SOIL ADSORBENT

Raytchev T.*[1]*, Filcheva E.*[1]*,
***Sokolowska Z.*[2]*, Hajnos M.*[2]

[1] *N. Poushkarov Institute of Soil Science, 7 Shosse Bankya Str., P.O. Box 1369, 1080 Sofia, Bulgaria*
[2] *Institute of Agrophysics, Polish Academy of Sciences, 4 Doswiadczalna Str., P.O. Box 201, 20-209 Lublin, Poland*

Abstract

Through thermal analysis of model organo-mineral samples, soil samples, and clay fractions (particle size <2 µm) and humic substances isolated from the studied soils, the relationship between genetic features of humus and its stability is traced. Simultaneously an attempt to define their stability fractions and their functions in formation of soil microstructure and properties is made.It was shown the manner of new-formed humus compounds during biochemical transformation of organic substances took part in the formation of organo-mineral nucleus of the soil adsorbent ($PM_{HS\text{-}clay}$). On the base of the concept of the natural modification of clay surfaces by soil organic matter the relationship between their steric features, activity and position on one hand and strength of connection with mineral part of the adsorbent, on the other. The result is distribution of the specific humus substances in different in their stability layers. It is performed a fractional scheme of humus substances, which report the connection between different degree of biochemical commitment organic fragments/mineral colloids with their oxidize stability and functional nature.

INTRODUCTION

Colloid-chemical nature of the passed processes between root system and soil adsorbent determine responsiveness to changes in the environment of their interactions. Sensitivity of soil colloids to these processes is defined of their quality composition and binding manner in the common organo-mineral structure. In principle their genetic features determine different participation of humus substances in the making, which reflects on the location and stability of their connection with mineral components of soil adsorbent (SA). This determines their stability to chemical and microbial attack.

In this paper the connection between genetic features of humus systems and their stability and it is made an attempt to group in different according to their stability fractions and defined of their functions in formation of soil microstructure and properties is presented.

Thermal analysis is mainly used in this study, which relatively well expressed the individual nature of humus substances with different origin. On the base of distinguished three structural units - aliphatic, aliphatic-cyclic and cyclic can assess the degree of aromatization and thermo stability of constructed components (Orlov, 1974, 1985; Raytchev et al., 1984a, 1984b). Limited indicativeness is a reason to develop a competitive investigations on possibility that method to be applied for measuring reliable data analyzing soil samples in their native state.

MATERIALS AND METHODS

Soils related to different taxonomy units with various particle size distribution, humus content, pH and CEC were included in this study. Samples of surface horizons of Eutric Vertisol, fine), (v.Sredetz – pH-H_2O 7.3; %C = 1.95; CEC = 27.8 $cmol.kg^{-1}$ – total cation exchange capacity); Haplic Chernozem, medium (v. Kochmar - pH-H_2O 6.5; %C = 1.48; CEC = 29.5 $cmol.kg^{-1}$); Haplic Luvisol, medium, (v. Slavyani - pH-H_2O 5.7; %C = 1.82; CEC = 23.9 $cmol.kg^{-1}$); Stagnogleyic Eutric Planosol, coarse, (v. Velchevo - pH-H_2O 4.5; %C = 1.38; CEC = 9.3 $cmol.kg^{-1}$) were analyzed.

Four types of treating were studied: no preliminary treatment (initial soil samples); treated by H_2O_2; saturated with humus substances; treated by H_2O_2 and humus substances. Thermal destruction of humic acids got: after straw decomposition (3 and 12 months); coal and studied soils was traced out (extraction procedure, Kononova, 1966).

An approach disparate from commonly used methods to prepare organo-mineral associations was accepted in the study. It is based on the saturation of the soil with new-formed humus substances during plant materials transformation (Raytchev, 1996). Plant materials (10 g) covered 10 g of the studied soil (initial or treated with H_2O_2) were pour on 100 ml distill water. Composting process was carried out in particular containers to separate solid phase for 60 days at 25°C. After this period organo-mineral suspension was watered with distill water and dry in a thermostat at 40°C.

Separately it is made an attempt to trace out the structural evolution of humic acids, isolated from disparate in genesis soils as Eutric Vertisol, fine and Stagny – gleyi - Eutric Planosol, coarse. Humic acids were extracted during straw decomposition process (3 and 12 months) and coal by extraction procedure (Kononova and Belchikova, 1961). Because of mineral part absences new-formed humus substances formed during straw composting were extracted with hot water and after that freeze dried.

Thermal analyze was carried out using equipment, system F. Paulik, J. Paulik and L. Erdey (Paulik et al., 1960). The working regime is as follows: rate of heating – 6^{o} min^{-1}; interval of heating - от 20 до 1000° C; galvanometer sensitivity - DTA – 1/10, TG - 200 mg of the scale; samples' weight - 0.5 g and 0.05 g respectively for soils and humic acids, both mixed with 0.25 g tempered Al_2O_3.

Energetic parameters were calculated according to the method of Turner and Schnitzer (Turner and Schnitzer, 1962; Van Krevelen et al., 1951).

RESULTS AND DISCUSSION

Theoretical analysis of derivatograms presented in Figure 1 and energetic parameters (Table 1) of the studied humic substances are based on the following facts:

1. There is a clearly expressed twist in the medium temperate region on TG-curves, due to decomposition of disparate components in humic acids' composition. This well corresponds to the statements of their bi- or three components' structure (Orlov, 1974).

2. Isolated humic acids after 3-months of straw composting are characterized with lower stability (temperature maximum - T_m of the corresponding reactions is moved to lower values) and with various composition (more number of reactions) compare to these described ones after 12 months of plant material humification.

3. Destructive interval in the high temperature region for humic acids, isolated from coal is around 3 times wider compared to this characterized humic acids extracted from composted straw. These differences, could presume, reflect the distinction of humic substances carbonization of both studied materials. Variety of easily distracted peripheric and aliphatic chains is bigger in water-soluble humic substances from composted straw, while coal humic acids are enriched with more stable heterocyclic compounds and aromatic nucleus.

4. The results presented in Table 1 show that similarity between humic acids, isolated from Eutric Planosol (EPl) and new-formed humic acids on one hand and identity of these extracted from Eutric Vertisol and coal on the other are very close.

5. The ratio between aliphatic and cyclic-nucleus structures constricted in the progress of humufication processes - increases portion of the last ones in the humic acids composition. This ratio decreases from 4.57 to 3.75 after several months of composting. If it is accepted humic acids, isolated from coal as representatives of the final phase of evolution, than in the frame of the formed interval could insert most of humic acids with different origin, evolution and degree of maturity. On this base comparing measured values, studied soils can be distinguished simply according to their degree of aromartization. There the evolution of humic acids, isolated from Eutric Planosol (Epl) is in advanced stage compared to the new-formed humic substances (respectively 1.87 and 3.75), but their aromatization is significantly lower in relation to this characterizes Eutric Vertisol (respectively 1.87 and 0.66). The degree of aromatization of Eutric Vertisols' humic acids is similar to measured values for coal humic acids (respectively 0.66 and 0.30). It can be assumed that they reached a completion phase of structural evolution. It have to be marked that the changes of these values will be with less leap character when are analyzed humic acids extracted from soils, belonging to one and the

same genetic class. This is related to their other characteristics. Similar interpretation for genetic and classification purposes are possible for higher taxonomy level.

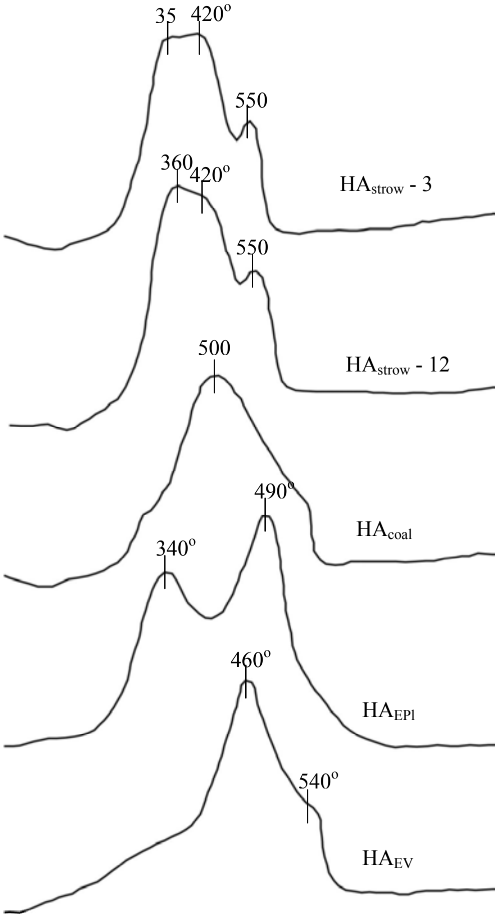


Fig. 1. *DTA curves of humic acids: straw - after 3 months (HA_{strow} - 3) and 12 months (HA_{strow} - 12) of humification; humic acids isolated from coal (HA_{coal}); humic acids isolated from Eutric Planosol (HA_{EPl}) and Eutric Vertsol (HA_{EV})*

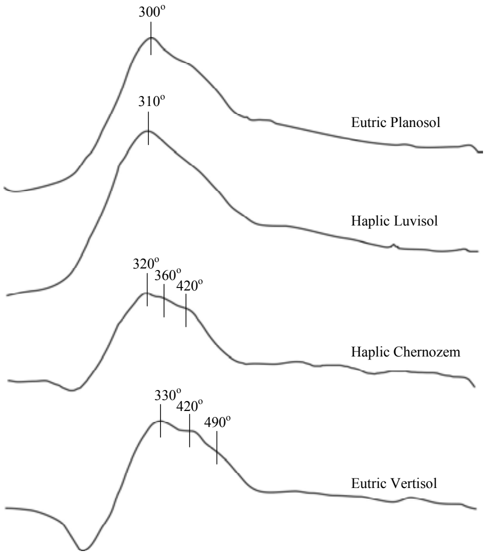


Fig. 2. *DTA curve of A horizon: Eutric Planosol (EPl) – v. Velchevo, Haplic Luvisol (HL) – v. Slavyani, Haplic Chernozem (HCh) – v. Kochmar, Eutric Vertisol (EV) – v. Sredets*

Table 1. Thermo-gravimetrical data (T_m, ^oC – temperature maximum of the reaction; ΔT - temperature interval of the reaction) and activation energy - E, kJ/mol; A/B, where A - low temperature region; B - high temperature region; ω – loss of weigh, mg) of exothermal effect of: (i) humic acids (HA) and ill – (particle size < 2μm), isolated from Eutric Planosol (EPl) and EutricVertisol (EV) and (ii) humic acids, isolated from straw (humufication 3 and 12 months) and coal.

Sample	A								
	I reaction			II reaction			III reaction		
	T_m, ^0C	ΔT	E, kJ/mol	T_m, ^0C	ΔT	E, kJ/mol	T_m, ^0C	ΔT	E, kJ/mol
HA from straw after 3 months	210	110	46.5	340	110	74.7	450	60	190.8
HA from straw after 12 months				305	190	38.5	420	100	105.3
HA isolated from coal							450	260	100
HA isolated from Eutric Planosol	270	130	49.8	340	110	74.7			
HA isolated from Eutric Vertisol				360	130	67.7	390	50	192.7
EPl – ill*				310	110	67.7	370	110	82.3
EV – ill*				290	90	77.1	430	100	108.1

Sample	ω_A, mg	B						ω_B, mg	$\frac{\omega_A}{\omega_B}$
		IV reaction			V reaction				
		T_m, ^0C	ΔT	E, kJ/mol	T_m, ^0C	ΔT	E, kJ/mol		
HA from straw after 3 months	32	480	40	310.2	540	60	241.1	7	4.57
HA from straw after 12 months	30				540	120	120.3	8	3.75
HA isolated from coal	8	560	90	350	620	90	381.2	27	0.30
HA isolated from Eutric Planosol	28	490	90	141.5				15	1.87
HA isolated from Eutric Vertisol	16	460	70	168.3	560	140	108.6	24	0.67
EPl – ill*									1.20
EV – ill*									0.75

*ω_{A} = loss of weight in II reaction; ω_B loss of weight in III reaction

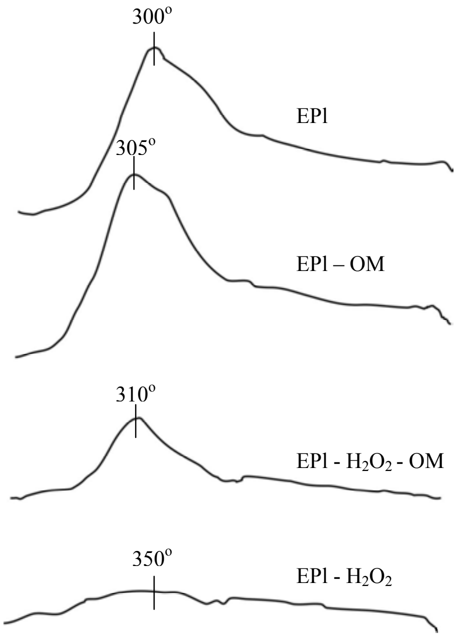


Fig. 3. *DTA curves of A horizon from Eutric Planosol – v. Velchevo: untreated soil (EPl); semple treated with humic compounds (OM) during humification process (EPl – OM); sample treated with H_2O_2 and saturated with OM (EPl - H_2O_2 - OM); sample treated with H_2O_2 (EPl - H_2O_2)*

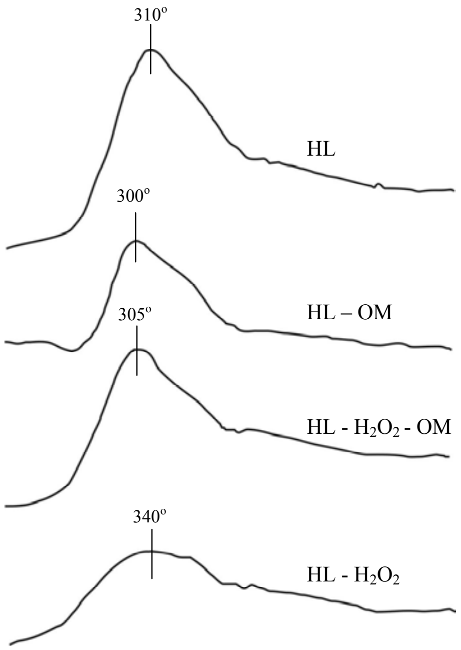


Fig. 4. *DTA curves of A horizon from Haplic Luvisol – v. Slavyani: untreated soil (HL); semple treated with humic compounds (OM) during humification process (HL – OM); sample treated with H_2O_2 and saturated with OM (HL - H_2O_2 - OM); sample treated with H_2O_2 (HL - H_2O_2)*

Analysis of thermogravimetric data (Figures 1, 2, 3, 4, 5, 6) and calculated energetic parameters, measured during thermal destruction of natural and model substances permit the following interpretation:

1. The exothermal effect for the studied soils is a result of passed two reactions in the low temperature region (190° – 400° C) and one in the high temperature region (370° – 560° C) of pyrolis, where both regions are relatively well distinguished in DTG, DTA and TG-curves of derivatograms.

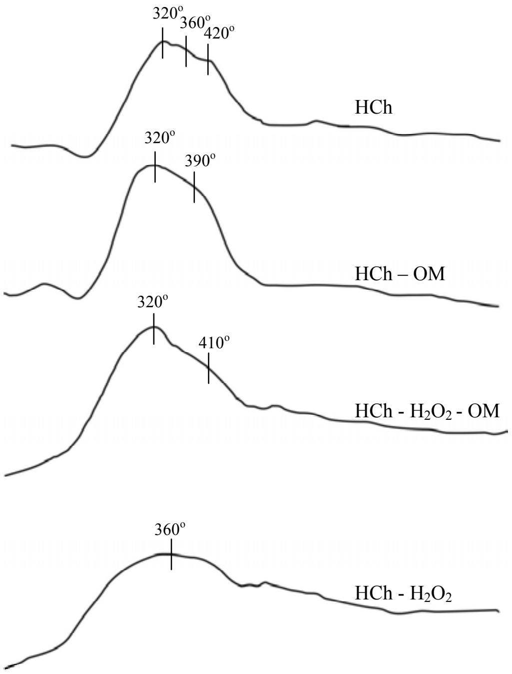


Fig. 5. *DTA curves of A horizon from Haplic Chernozem – v. Kochmar: untreated soil (HCh); semple treated with humic compounds (OM) during humification process (HCh – OM); sample treated with H_2O_2 and saturated with OM (HCh - H_2O_2 - OM); sample treated with H_2O_2 (HCh - H_2O_2)*

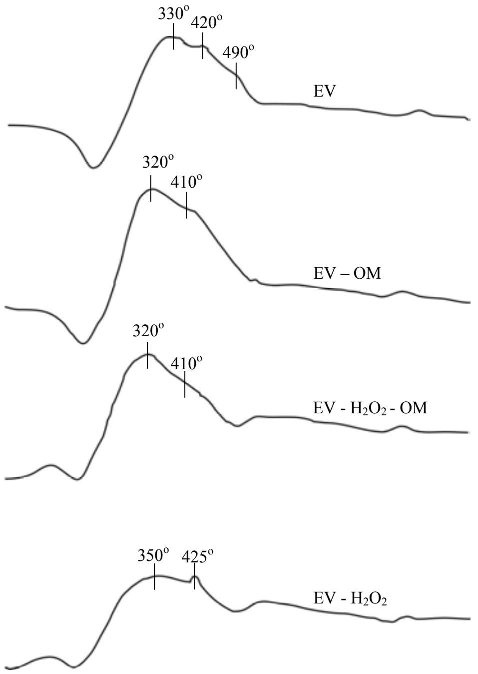


Fig. 6. *DTA curves of A horizon from Eutric Vertisol – v. Sredetz: untreated soil (EV); semple treated with humic compounds (OM) during humification process (EV – OM); sample treated with H_2O_2 and saturated with OM (EV - H_2O_2 - OM);sample treated with H_2O_2 (EV - H_2O_2)*

2. The value of activation energy (E) of first low temperature reaction does not differ substantially for the fourth studied soils. It was established some varieties concerning the second reaction. It is observed the highest and less activation energy for Eutric Vertisol (141,5 kJ/mol) and Eutric Planosol (40,0 kJ/mol), respectively.

3. It is observed the relatively widest interval of destruction (160^o) and the highest value of temperature maximum (T_m) in the high temperature region for Eutric Vertisol. The last one and the presence of deviations in smooth way in DTG - curvre are indications for complexity of this reaction (Chernikov and Konchitz, 1973). It could presume that the variety of more stable components is larger (Eutric Vertisol).

4. The second low temperature reaction passes in a narrow temperature interval, where E reaches the highest values. This is probably due to destruction of bonds between low molecular humus substances and amorphous forms of iron and aluminum (Dubin, 1970).

5. On the base losses of weigh in both temperature regions, the investigated soils form the descending order: Eutric Vertisol (1.1) > Haplic Chernozem (0,8) > Haplic Luvisol (0,7) > Eutric Planosol (0,4), as a rezult of aromatic share (ω_B/ω_A) in the soil organic matter structure.

Position of the both final numbers in this order corresponds to the result of studied humus substances, isolated from these soils (Eutric Vertisol and Eutric Planosol). Study on their structural-adsorption characteristics, presented stronger bonding of humus substances with montmorillonite compared to kaolinite minerals and hydro-mica confirmed these results.

Since mineralization and humus formation processes pass simultaneously and continuously, traced out the changes in thermo stability of organic matter in additional enrichment with new fractions represent significant interests. Resembling real processes of some extend could be made by saturation of initial soils with humus substances of similar type through humification of plant materials on mineral mass. The results of thermal analysis of prepared samples (Table 2 and Figures 3, 4, 5, 6) show that partly as in thermogravimetric data and values of energetic parameters well expressed in the second reaction of low temperature region. It is interesting to mention that soils manifest some selectivity to adsorb humus substances, which are in luck. For example Eutric Planosol is enriched with more thermo stable components, while Haplic Chernozem accepts components with aliphatic nature.

In order to distinguish the action of additional humus substances it is necessary to establish interaction with soil organic matter. An experiment with consequently treatment with H_2O_2 and saturated with humic substances soil samples was carried out.

The results of thermal analyze of studied samples (Table 2 and Figures 3, 4, 5, 6) could be generalized as follows:

1. First low temperature reaction disappears after treatment with H_2O_2, E values significantly decrease for second reaction and temperature interval of destruction increase. There is a base to assume that products formed during treatment are destroyed there (Dubin, 1970). This can be accepted as confirmation of the hypothesis on destruction of bonds between low molecular humus substances and amorphous forms of iron and aluminum.

2. After saturation of such treated samples, losses of weigh in the exo-effect is similar for studied soils and differences in the ratio of both humus fractions decreases. The highest value corresponds to Eutric Planosol and lowest one - to Eutric Vertisol, respectively, probably due to their different mineral composition.

Table 2. Thermo-gravimetrical data (T_m, ^oC – temperature maximum of the reaction; ΔT - temperature interval of the reaction) and activation energy (E, kJ/mol; A/B, where A - low temperature region (I + II reactions); B - high temperature region (III reaction); ω_A - loss on ignition in low temperature region; ω_B - loss on ignition in high temperature region) of exothermal effect of Eutric Planosol (EPl), Haplic Luvisol (HL), Haplic Chernozem (HCh), and EutricVertisol (EV). NT- untreated samples, OM – samples treated with humic compounds during humification process; HP - samples treated with H_2O_2, OP – both last treatments together. $R=\omega_A/\omega_B$. The sequence of symbols corresponds to the respective treatment.

Soil /Treatment		I reaction			II reaction			III reaction			ω_A, mg	ω_B, mg	R
		T_m	ΔT	E	T_m,	ΔT	E	T_m	ΔT	E			
E P	NT	270	100	64.4	320	70	40.0	410	140	72.8	26	10	2.6
	HP				300	180	154.2	420	120	87.4	12	9	1.3
	HM	270	167	40.4	320	50	132.5	390	150	63.9	21	11	1.9
	OM	270	110	58.8	340	70	117.5	410	140	72.8	24	18	1.3
H L	NT	280	120	55.9	320	60	128.3	410	150	68.2	30	20	1.5
	HP				340	210	39.0	240	110	95.4	11	13	0.8
	HM	270	120	53.6	320	70	110.0	410	150	68.6	18	14	1.3
	OM	270	100	64.4	330	80	110.0	420	150	70.0	32	23	1.4
L C	NT	280	120	55.9	340	70	117.5	420	140	75.2	23	18	1.3
	HP				310	140	53.1	420	150	70.0	7	15	0.5
	HM	280	140	47.9	330	60	132.5	420	140	75.2	17	13	1.3
	OM	280	130	51.7	360	70	125.5	430	140	77.1	34	19	1.8
E V	NT	300	120	59.7	350	60	141.5	440	160	69.6	28	30	0.9
	HP				350	160	53.1	420	70	150	12	14	0.8
	HM	280	90	74.3	330	60	132.5	410	120	85.1	17	16	1.1
	OM	290	90	77.1	350	70	121.3	430	150	75.2	33	31	1.0

The indicatives of data obtained for initial soil could verify comparing the results for clay fractions (Table 1). They referred to group transitionally-porous minerals adsorbents with predomination of fine ones in the structure of Haplic Chernozem. It is typical for derivatograms obtained disappearing of one of the low temperature reaction and moving of T_m toward higher temperature for both reactions. The interpretation of the results is facilitated, but it is not applicable for natural soils. This is logic, because during extraction of soil colloid particles, it is possible to eliminate some easily soluble components of humus substances. Part of it is stable bonded in bigger aggregates with clay minerals, which is unextracted. Dispersion of this relatively stable bonded organo-mineral association to colloid sizes during extraction procedure is no completed and most of them retain in larger fractions.

On the base of the rate of oxidation and thermal stability soil organic matter of both soils Eutric Planosol and Vertisol could assign to the opposite types of plants transformation: initial stage of humification and maximum aromatization, respectively. High bio-chemical activity leads to braking off the peripheral chains from the molecules of humic acids and accumulation of the most stable components. Fulvic acids, which are more available to microorganisms, decrease. Podzolic soil, characterized with lower bio-chemical activity, and consist humic acids enriched with peripheral chains and fulvic acids with carbon. This reflects to the ratio Ch/Cf. Analiysis of more number of soil samples from the main soil types of Bulgaria confirm the genetic affiliation and evaluation nature (samples of A-horizon: stagny - gleyi - Eutric Planosol, coarse - v.Vrabevo, v.Velchevo, v.Dushevo and Lovni dol; Haplic Luvisol - v. Slavyani and v. Nikolaevo; Luvic Phaeozem- v. Grivitsa, v. Bejanovo and Isperih; Chromic Luvisol - v. Krepost, v. Grigorevo and v. Sadievo; Haplic Chernozem, medium - v. Kochmar, v. Bosilkovtsi and town G. Dabnik; Eutric Vertisol, fine - v. Sredets and v. Skalitsa - profiles NN 42 and 66). Thermogravimetral data and calculated energetic parameters (measured during thermal destruction of natural and model substances) show: (i) with the increasing of humic acids portion in soil organic matter composition, thermo stability of humus system enhance, (ii) starting temperature of termo destruction arises from 150^{o} to 230^{o} C in the order presented in Table 3:

Table 3. Ratio(A/B) between low (A) and high temperature treated (B) fractions of humus substances in the studied soils

Soil Type (FAO, 1997)	A / B
Eutric Planosol	2.0
Haplic Luvisol	1.4
Luvic Phaeozem	1.2
Chromic Luvisol	1.0
Haplic Chernozem	0.8
Eutric Vertisol	0.6

Well-expressed relationship between stability and genetic features in the humus structure is grounds to accept thermal analysis as an appropriate one in analyzing components of soil organic matter with no preliminary extraction, followed by destruction of soil samples. It could be accepted that during thermo destruction a fractionation accomplished, but the identification of their structural components is complicated or even impossible. This needs a preliminary extraction and analyzing of humus substances where the disadvantages of the applied methods and changes of the native state of the studied samples are occurred.

Established changes in the stability of humus system in the course of treating show, that their sensitivity towards thermo destruction is determined by condition where primary organo-mineral nucleus ($PM_{HS\text{-}clay}$) is formed. Its inorganic matrix is a natural mixture of clay minerals. Soil organic matter (HS_{clay}) naturally modify its surface with participation of hydroxides, especially those of Si, Al and Fe. On the surface of these colloid formations are bonded potential determined ions of nucleus (-OH, PO_4^{3-}, SiO_4^{2-}, -COOH etc.), and in the part of stationary and entire diffusion layer are distributed compensated ions (exchangeable cations) of colloid system. Additional adsorption centers (part of this is organic component of the system) are disclosure on the formed structure of organo-mineral nucleus.

Stereo features are formed in the initial stages of decomposition of death plant and animal residues, included in the solid phase of their bio-chemical transformation. Components of soil organic matter, which are not involved in these processes, are refereed to this phase. Intermediate products, formed during the elementary parallel, induction, and sequential reaction catalyze the following ones namely between main sources of humus substances and natural humus substances. Their different thermo destruction rate and constant synthesis started in each stage of destruction leads to formation of semiliquid phase. It contains products, released by enzymes, and which have high activity and colloid-chemical properties. It could presume that an intermediate phase originates contained biological mixture of substrate and enzymes in different state of biochemical commitment (Figure 7).

When export of intermediate products absence, it is created favourable conditions for parallel reactions of synthesis. This leads to formation of specific humus substances and corresponding destruction. Domination of mineralization processes will exclude the carbon mass out of the system and this would transmit a subside type of the wave character of common cycle of the transformation. In chemical point of view, group of unstable organic compounds (its content changes fast) contains unspecific compounds, hydrocarbons, polypeptides, lipids, chlorophyll, and pigments. It could be expected that microorganisms consumed it as source of energy and reserve of nutrients. Humic acids, fulvic acids, partly lignin and polysaccharides, are referred to more stable substances.

It is necessity to indicate, that simple static concept of molecular structure is not applicable for humus macromolecules. This concept has to be accepted in wider significance i.e. including not only process of formation, but their different dynamic behavior. This is not a chance it is an integral characteristic of bio-molecules that determine its dynamic structure and biological function. The most important steric features of these high moleculer formations are connected with flexibility of the chain. The last one decreases with enhancing with both, number of the polar groups and size of the steric net. This property is of great importance, allowing formation of "clatrat" compounds, where molecules are bounded mechanically, thanks to its steric configuration. Elasticity and high activity of the organic fragments facilitate formation of stable adsorption - solvate layers on the mineral colloids' surface, constructed the organo-mineral nucleus of soil adsorbent.

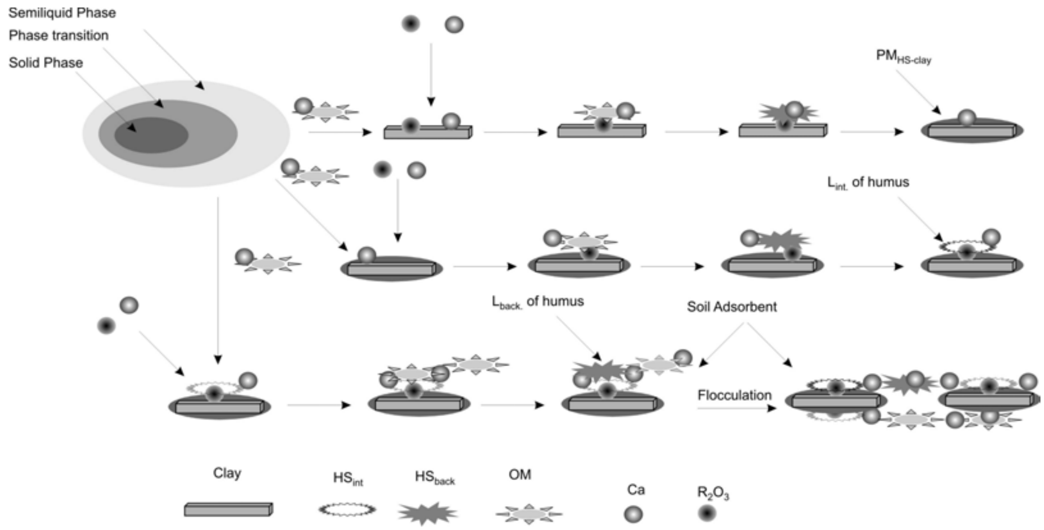


Fig. 7. *Formation of primary organo-mineral matrix ($PM_{HS\text{-}clay}$) and distribution of organic layers ($L_{int.}$ and $L_{back.}$)) in the Structure of Soil adsorbent (SA) $HS_{int.}$ – humus substance from interaction layer of Soil adsorbent; HS_{back} - humus substance from back layer of SA; OM – neoplasme of humus substance during humification process of oak leaves.*

New organic molecules ($HS_{back.}$), could be sorbed on this stabilized organo-mineral layer via polyvalent ions and surfaces with polymerized units with highly performed aromatic character ($HS_{int.}$) are formed. The result is unify specific humus substances in different in their stability fractions which reflect their genetic features.

The investigation on kinetic of oxidazable thermodestruction shows that the progress of that process depends on the stability of the components corresponding to their structural features. The results obtained give a reason to define two hidhly differentiated humus fractions according to their thermal stability marked as A and B. Fraction A includes mainly organic compounds with aliphatic structure enriched in OH, COOH and other functional groups. These can be connected to the aromatic compounds as well. It is the most dynamic part of the humus and organic substances received into the soils. The humus substances of fulvic type enriched in OH and

COOH groups as well as the organic substances which components are in the initial stage of humification are included in fraction A. Because of its instability and specific susceptibility to the changes in the environment this fraction gives a dynamic character of the properties of the colloidal soil formations. The degradation of fraction A needs relatively low energy.

"Srtuctural" determined fraction B is formated mainly by aromatic compounds and components of the humus compounds with maximal degree of aromaticity. If the conditions for their formation are changed, part of its components could be stabilized and the other part - disintegrate to more unstable components. The latest one gives the possibility to natural transfusion from one to another combination. Formation of organo - mineral compounds and the high oxidation state stabilises fraction B to biodegradation. This fraction is structural formation and stabilized colloid-chemical state of soil adsorbent. Their typical representatives are humin (unextractable carbon) and compounds that are in the composition of anthracite. More energy is needed to destroy fraction B.

On this base a method for realization the fractional scheme was developed. The defects of the extraction methods and the limitations in the thermal analysis are avoided by study the kinetics of the process analysing samples in their native state.The analysis during the destruction reduce the risk of changes in their native state. (Raytchev, 1996; Raytchev T. et al., 1993). Comparative study was carried out in order to clarify its possibility. Samples of surface horizons of leached smolnitza (Eutric Vertisol, FAO), grey forest soil (Haplic Luvisol, FAO), light grey forest soil (Eutric Planosol, FAO) and coal were analysed (Raytchev, 1992). The studied soils are related to the different taxonomy units and varied in humus content, particle size distribution, pH and CEC. These samples are analyzed according to the method of Kononova-Belchikova (Kononova, 1966) and ratio between fraction of humic and fulvic acids (Cf/Ch) were determined. Using DTA method the proportion between low- and high temperature fractions - A and B was measured. Data obtained were compared with ratio C_A/C_B, where C_A is organic carbon content of labile fraction and C_B is organic carbon content of high oxidize fraction (Table 4).

The adequate of proposed fractional scheme is proved via similar results obtained, analyzing samples applied methods mentioned above (Raytchev, 1992).

An additional indication for application of this method in the condition of Na salinity is absence of high oxidize components in the humus system, specific for sodium-sulfuric solonchak-solonetz (Plovdiv region). This is in correspondence with its genesis - alkali reaction does not allow formation of stable organic structure and humus substances are presented as soluble sodium fulvates.

Table 4. Parameters of soil organic matter and coal

Soil type (FAO, 1997)	C, %		T_M, ^0K	C_A, %	C_B, %	C_A/ C_B	C_f/C_h	C_h/C_f
	I	II						
Light Grey forest soil (Eutric Planosol)	0.990	1.090	381.68	0.81	0.18	4.5	4.2	0.24
Grey forest soil (Haplic Luvisol)	1.034	1.039	379.51	0.75	0.28	2.7	1.9	0.54
Leached Smolnitza (EutricVertisol)	1.880	1.750	380.37	1.13	0.75	1.5	0.3	3.26
Coal	38.40		380.37	10.3	28.1	0.4		

Soil type (FAO, 1997)	w, %	F	humus, %		N
			1.724	F	
Light Grey forest soil (Eutric Planosol)	-10.1	1.565	1.71	1.55	0.100* 0.096**
Grey forest soil (Haplic Luvisol)	-0.5	1.716	1.78	1.77	0.120 0.112
Leached Smolnitza (EutricVertisol)	+6.9	1.836	3.23	3.45	0.150 0.130

I - C content in studied sample, corresponding to CO_2 *measured during destruction processes; II - C content in studied sample, measured according* CO_2*,released as a result of reduction of oxide agent excess; * - nitrogen content (Kjelhdal method), measured in the equipment, after ending the destruction; ** - nitrogen content (Kjelhdal method), measured after destruction (microchromatic method of Turin)*

$$F = \frac{172.414}{100 - W(\%)}$$

CONCLUSIONS

Dynamic character of new-formed organic structure in the coarse of biochemical transformation of plant materials is reflected on their colloid-chemical behavior Elasticity and high activity of the organic fragments facilitate formation of stable organo-mineral nucleus of soil adsorbent ($PM_{HS\text{-}clay}$).

It represents a natural mixture of clay minerals, which surface is naturally modified by soil organic matter (HS_{clay}) with participation of hydroxides, especially those of Si, Al and Fe.

Steric features of humus substances and high activity of their components in the formation moment determine stability of binding with mineral adsorbent.

New organic molecules ($HS_{back.}$), could be sorbed on this stabilized organo-mineral layer via polyvalent ions and surfaces with polymerized units with highly performed aromatic character ($HS_{int.}$) are formed. The result is unify specific humus substances in different on their stability fractions which reflect their genetic features.

Different degree of biochemical commitment organic fragments/mineral colloids determine the connection between their oxidize stability and functional nature, which is a base for fractional scheme of humus substances.

REFERENCES

Chernikov, V. A., V. A. Konchitz, 1973. Kinetic of the pyroliz of fulvic compounds from some soil types Proceedings of the Timiryazev Agricultural Academy, 1, 101-113. (Ru).

Dubin, V. N., 1970. Thermogravimetral characteristics and kinetik parameters for thermo destruction of humus acids of the main soils in Moldavia. Soil Science 9, 70-87. (Ru).

FAO – UNESCO. 1997. Soil Map of the World. Revised Legend, ISRIC, Wageningen.

Kononova M.M., 1966 Soil organic matter. It's nature, it's role in soil Formation and Soil Fertility. 2nd English Ed., Pergamon Press Inc., Elmsformd M.V., 544 pp.

Kononova, M. M., N. P. Belchikova, 1961. Accelerated methods for determination of humus composition of mineral soils, Soil Science, 10, 75-87 (Ru).

Orlov D. S., 1974. Soil humus substances. Univ. of Moscow Ed., Moscow, 333 pp. (Ru).

Orlov, D., 1985. Soil chemistry. Univ. of Moscow Ed., Moscow, 376 pp. (Ru).

Paulik, F., J. Paulik, L. Erdey, 1960. Der Derivatograph, Bergakademie, 12, p. 413-416.

Raytchev, T., 1992. Method of fractionation of soil organic substance and of identifying structural components in the course of their oxidation destruction, Soil Science, Agrochemistry and Ecology, Sofia, vol. XXVII, 1: 22-27. (Bg).

Raytchev, T., 1996. Influence of organo-mineral interactions on colloid-chemical state of the soil adsorbent. D. Sci. Thesis, “N. Poushkarov” Inst., Sofia, 161 pp. (Bg).

Raytchev, T., D. Donov, I. Athanassov, 1984a. Study of the humus substances in soil by using the thermal analysis, Soil Science and Agrochemistry, Sofia, vol. XIX, 3:35-43. (Bg).

Raytchev, T., P. Konishev, D. Donov, 1984b. Application of thermal analysis in the studies on the structural evolution of humic substances, Soil Science and Agrochemistry, Sofia, vol. XIX, 4:82-87. (Bg).

Raytchev T., N. Mitsulov, E. Filcheva, I. Uzunov.1993. Method and measuring system for determining content and the rate of intermolecular oxidation of easily and hard oxidize fractions of soil organic matter. Reg. n 87642/14.03.1989, Bulletin N 10/15.10.1990, Invention certificate 47906/10.06.1993, Sofia, Bulgaria. (Bg).

Turner, R. C., M. Schnitzer, 1962. Thermogravimetry of the organic matter of a Podzol, Soil Sci., 93, 4, p. 225-232.

Van Krevelen, D. W., C. Van Heerden, F. J. Huntjens, 1951. Physico-chemical aspects of the pyrolysis of coal and related organic compounds, Fuel, 30, p.253-259.

DIFFERENCIES IN STABILITY OF SOIL ORGANIC MATTER FRACTIONS DURING THERMO-OXIDIZABLE DESTRUCTION

Raytchev T.[1], Filcheva E.[1],
Hajnos M.[2]., Sokolowska Z.[2]

[1] N. Poushkarov Institute of Soil Science, 7 Shosse Bankya Str., P.O. Box 1369, 1080 Sofia, Bulgaria
[2] Institute of Agrophysics, Polish Academy of Sciences, 4 Doswiadczalna Str., P.O. Box 201, 20-209 Lublin, Poland

Abstract

Reported is a method and a measuring system of fractionating the soil organic matter. The method suggested offers a possibility to determine the ratio of easily- and hardly-oxidizable fractions, as well as the carbon content, nitrogen and degree of their intramolecular oxidation through direct analysis in the course of the soil organic substances destruction, performed successfully in two soil samples without preliminary chemical treatment. This excludes the effect of chemical reagents and atmospheric CO_2, and creates conditions for automatization and reduction in the process duration. The development of the system is original and is protected by an inventor's certificates.

Examination of the kinetics of humus compounds oxidative destruction is carried out with potassium dichromate in sulfuric acid media at constant temperature (maintained in a thermostat within 100^0-160^0 interval), and under continuous at constant gas flow rate, the gas being cleaned of CO_2. Under these conditions the destruction process takes gradual course depending on the stability of the structural fragments. The amount of these fragments is determined by the data obtained through synchronous measurement of temperature in a reaction vessel, and of CO_2 amount released at carbon oxidation, the carbon forming of soil humus substances, with the aid of known equations, describing the kinetics of reactions of first order.

INTRODUCTION

The defects of the extraction methods and the limitations in the thermal analysis are avoided by study the kinetics of the process analysing samples in their native state.The analysis during the destruction reduce the risk of changes in their native state. (Raytchev, 1996; Raytchev et al., 1993). Process of thermo-oxidize destruction is traced out in mixture of potassium dichromate and sulfuric acids medium under both, continuous increase of temperature and at constant gas flow rate, the gas being cleaned of CO_2 (Raytchev and Filcheva, 1989; Raytchev, 1992; Raytchev et al., 1993a, 1993b; Uzunov et al., 1995).

Under these conditions the destruction process takes gradual course depending on the stability of the structural fragments. The amount of these fragments is determined by the data obtained through synchronous measurement of temperature in a reaction vessel, and of CO_2 amount released at carbon oxidation, the carbon forming of soil humus substances, with the aid of known equations, describing the kinetics of reactions of first order.

THE METHOD

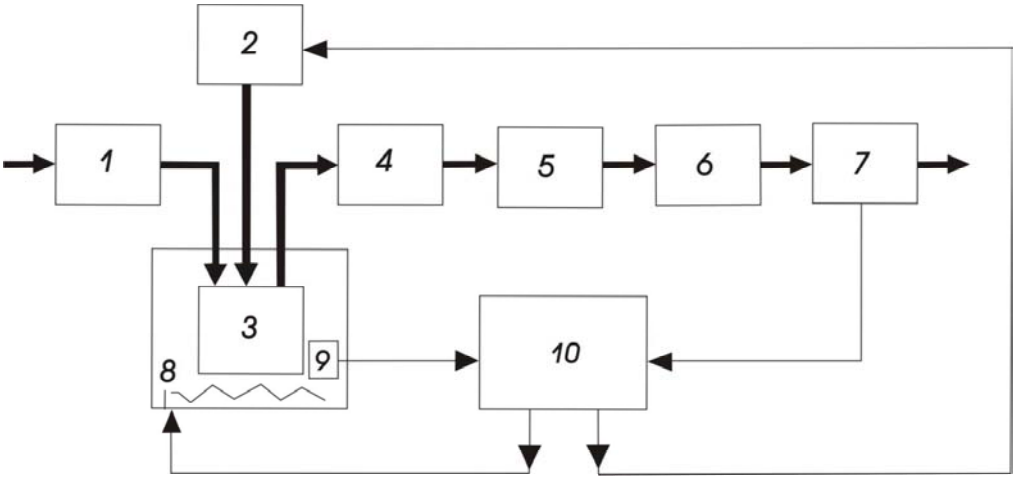
According to proposed method, soil sample is placed into the reaction vessel and oxidative destruction is carried out with potassium dichromate in sulfuric acid media at constant temperature (maintained in a thermostat within 100^0-160^0 interval), and under continuous at constant gas flow rate, the gas being cleaned of CO_2. Under these conditions the destruction process takes gradual course depending on the stability of the structural fragments. The amount of these fragments is determined by the data obtained through synchronous measurement of temperature in a reaction vessel, and of CO_2 amount released at carbon oxidation, the carbon forming of soil humus substances, with the aid of known equations, describing the kinetics of reactions of first order.

In the same soil sample the degree of intramolecular oxidation can be determined (Raytchev and Filcheva, 1989; Raytchev et al., 1993a). According to classic methods it is calculated by the difference between the content of total organic carbon by both methods Knop-Sabanin's or Guvstanson (Orlov and Grishina, 1981; Kononova, 1966) and carbon content, determined with Turin's one or its numerous modifications (Orlov and Grishina, 1981; Kononova, 1966; Nelson, and Somlers, 1982; Filcheva and Malinova, 1995; Uzunov, 1993; Raytchev et al., 1993a, 1993b). It is needed to be analyzed two parallel samples in each of the mentioned variants. There exists another calculated method based on the results of elements' analysis, applied for pure compounds or isolated from natural organic mixtures.

According to the Turin's method, carbon content is determined by the quantity of the oxidizer (potassium dichromate in sulfuric acid media) consumed for the oxidation of organic carbon in the samples. The amount of consumed oxidizer is determined by titration with solution of $FeSO_4.(NH_4)_2SO_4$. The disadvantages of the method are related to enhanced results due to both, susceptible to oxidation compounds of Fe, Mn, Cl and reduction character of organic matter. Lower values for carbon content are measured in the cases with atomic ratio $H : O < 2$.

Knop-Sabanin's method (Orlov and Grishina, 1981; Kononova, 1966) avoids some of the mentioned disadvantages, but this method performs low efficiency and precise cleaning of released CO_2 trough several absorbers. Because of complicated procedures this method has no wide application, despite the received data on organic carbon are comparable to those measured using Gustavson's method. The last one is based on the heating process at temperature 700° - 750° C and constantly blows through with O_2 in the presence of CuO. CO_2 released in the process of destruction is measured gravimetrically.

A structural scheme of the measuring system is designed to realize the method where the disadvantages of the mentioned above procedures are avoided (Scheme 1).



Scheme 1. *Structural scheme of a measuring system for determining the humus content of the soil* ***1*** *-* CO_2 *- adsorber;* ***2*** *- dosing unit;* ***3*** *- reaction vessel;* ***4*** *- condenser;* ***5*** *- air pump;* ***6*** *- flow rate rotameter; 7 -* CO_2 *gas analyzer;* ***8*** *- thermostat;* ***9*** *- thermosensor;* ***10*** *- microcomputer and analogue-digital converter*

The soil analysis runs as follows: an amount of soil sample containing not more than 10 mg of organic carbon (usually 100 to 700 mg of soil sample, sieved trough 0.25 mm openings) is placed into the reaction vessel (3), and with air pump (5) maintained constant flow rate (60 l/h) gas cleaned of CO_2, and the pneumatic channel is scavenged until the gas analyzer scale reads zero. A mixture of potassium dichromate and sulfuric acid ($K_2Cr_2O_7$: conc. H_2SO_4 1:1) is added trough dosing unit (2) and the reaction vessel (3) is moved into the thermostat (8) at 160° C. The instantaneous value of CO_2 released in the process of destruction is measured by gas analyzer (7) and recorded by computer (10).

The organic carbon content is calculated by equation (1):

$$C = K \int_{t_1}^{t_2} CO_2(t)dt, \qquad (1)$$

where C is the total organic carbon in percentage of the soil sample weight; *K* - the weigh coefficient readings molecular weight of CO_2 and atomic of C and soil sample weight; t_1 and t_2 - the initial and final moments of the process.

The rate of the intramolecular oxidation of the humus compounds is determined when the thermooxidative destruction is over. An excess of carbohydrates (concentration 1 mg/ml C) is added in the reaction vessel and by the amount of CO_2 released the oxidizer remained is determined.

The rate of the intramolecular oxidation is calculated by equation (2):

$$W(\%) = \frac{C_{CO_2} - (C^0 - C'_{CO_2})}{C_{CO_2}} \qquad (2)$$

where C_{CO_2} is the amount of total organic carbon when the oxidative destruction is over; C^0 - the amount of organic carbon equal to the initial quantity of an oxidizer; C'_{CO_2} - the amount of organic carbon equal to the excess quantity of an oxidizer

The coefficient 1.724 is used to transfer organic carbon to humus, based on the assumption that humus contains approximately 58 % C:

$$F = 100 / 58 = 1.724 \qquad (3)$$

Carbon content in humus varies significantly (Krastanov et al., 1986) and how much these values differ from the mean ones, the error in calculations will increase. Consequently, it is necessary to use differentiated coefficients on the base of intramolecular oxidation calculated by the proposed equation (4):

$$F = \frac{100}{58 - \frac{58.\%\omega}{100}} = \frac{172.414}{100 - \%\omega} \qquad (4)$$

Results of this experiment published in 1989 (Raytchev and Filcheva, 1989) statistically proved the advantages of described method and allow us to recommend as accuracy and precise method for humus measuring, with error less than 3 % (Tab. 1).

In the same sample when the excess of oxidizer in the reaction vessel is compensated with carbohydrate addition, total nitrogen can be determined after distillation according to Keldhal's method. The reaction conditions are similar to these of Turin's micro-chromic method (Orlov and Grishina, 1981). The method suggested offers a possibility to determine the carbon content, nitrogen and degree of their intramolecular oxidation through direct analysis in the course of the soil organic substances destruction, performed successfully in one soil samples without preliminary chemical treatment.

Table 1. Carbon content in the studied soils ($\bar{x}+\Delta x$)

C, %	$\bar{x}+\Delta x$	C, %	$\bar{x}+\Delta x$
Haplic Chernozem (G. Dabnik)		*Eutric Planosol (v.Velchevo)*	
1.02		0.87	
1.02		0.89	
1.00	1.01 ± 0.028 S=0.023	0.90	0.087 ± 0.030 S=0.031
0.98		0.88	
1.04		0.82	
Haplic Luvisol (v. Slavyani)		*Eutric Vertisol (Sredetz)*	
1.30		1.79	
1.33		1.74	
1.30	1.30 ± 0.043 S=0.035	1.69	1.75 ± 0.045 S=0.036
1.24		1.76	
1.32		1.75	
Eutric Planosol (v. Vrabevo)		*Dystric Planosol (v. Otez Kirilovo)*	
0.91		0.34	
0.94		0.38	
0.91	0.092 ± 0.019 S=0.015	0.34	0.37 ± 0.046 S=0.037
0.90		0.37	
0.92		0.43	

Statistical characteristic of the proposed method					
Sdev	Sdev Var.	Conf. Interv.	Variab. coeff.	Coeff. of variance	Reproduc.
0.03	±0.009	$(x\pm0.063)\%C$ P=0.95 f=24	$\bar{x}$=3.7	S=$\pm$ 3.15	96.85 %

Designed method and a measuring system give the possibility of fractionating the soil organic matter. The method suggested offers a possibility to determine the ratio of easily- and hardly-oxidizable fractions, successfully in one soil sample without preliminary chemical treatment. This excludes the effect of chemical reagents and atmospheric CO_2, and creates conditions for automatization, and reduction in the process duration. Realized CO_2 is measured in 1 s interval.

This paper presents the result of application of this method analysing samples of different in their genesis soils. Samples of surface horizons of leached smolnitza (Eutric Vertisol, FAO), grey forest soil (Haplic Luvisol, FAO), light grey forest soil

(Eutric Planosol, FAO), and coal were analysed (Raytchev, 1992). The studied soils are related to the different taxonomy units and varied in humus content, particle size distribution, pH and CEC. These samples are analysed according to the method of Kononova-Belchikova (Kononova, 1966) and ratio between fraction of humic and fulvic acids was determined.

Using DTA method the proportion between low- and high temperature fractions: A and B was measured. Data obtained were compared with ratio C_A/C_B, where C_A = organic carbon content of labile fraction and C_B organic carbon content of high oxidise fraction. The total organic carbon is determined according to Turin's microchromic method. Humus content is calculated using both coefficients: F = 1.724 and those using based on the data of intramolecular oxidation, equation 4 (Tab.2).

Calibration of the system is made with saccharose as water solution, concentration 1.5 mg C / ml as follows:

In the reaction vessel (3) poured part of the saccharose solution, containing 3 mg C, and the system is scavenged with gas (cleaned of CO_2) until the converter (9) CO_2 - electrical signal reads zero. 10 ml mixture of potassium dichromate and sulfuric acid ($K_2Cr_2O_7$: conc. H_2SO_4 1:1) is added trough dosing unit (2) and the reaction vessel (3) is moved into the thermostat (8) at 160^o C. Process of destruction is controlled through the converter (9) CO_2 - electrical signal and instantaneous value of CO_2 released from the initial up to the final point in the process of destruction is measured by gas analyzer (7) and recorded by computer (10). The process is over after the converter (9) reads zero.

Data obtained and calculated parameters according to formulas 1 to 8 (Application 1) give the possibility for graphically study on the relatively change of the rate constant with the variation of temperature in the reaction vessel (Fig. 1). Curve presented follows equation 5, and evidence for this is it changes to linear ones in the case of a semi logarithmic scale, according to equation 6.Constant C in formulas 5 and 6 is determined by two end points co-ordinates in the curve. Absence of "twist" on the curve is in accordance with the nature of studied substance - saccharose. The high value of correlation coefficient $r = 0.9953$ proves the minimum deviation of experimental from the theoretical curve.

On the base of revised published papers on the possibilities to study the humus structures' stability with the methods mentioned above grounds us to carried out a competitive experiment with soil samples, humus substances and coal dust, which contain humus substances of final maturity (Raytchev, 1992) (Tab. 2).

Fractionation of soil organic matter is accomplished in the same way. Instead of saccharose solution in the reaction vessel (3) is placed studied soil sample of Eutric Verisol, sieved trough 0.25-mm openings (Fig. 2). A "twist" is observed on the experimental curve. When equation 6 is applied and two end points on the integral curve are used, even the results are pointed in a semi logarithmic scale, the experimental curve is not changed to linear one.

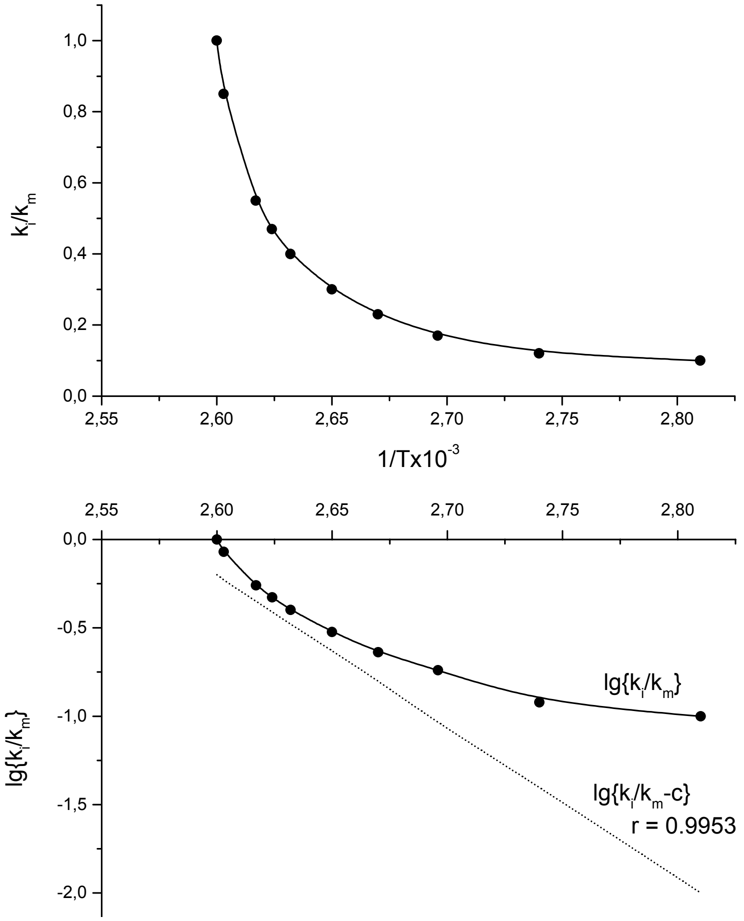


Fig. 1. *Relative change of the rate constant* (K_i / K_m) *with the temperature* $(-1/T^{10-3})$ *during oxidative destruction of saccharose*

The studied curve is examined as constituted of two crossed curves and equation 6 is applied for each one. Correlation coefficients $r = 0.9998$ and $r = 0.9918$, correspond to the curves, described the destruction of easily- and hardly oxidizable fractions, show a relatively negligible deviation - experimental from the theoretical curve. The co-ordinates of the cross point, so called "point M" are determined by linear regression. Distracted to this moment organic substance corresponds to the content of easily oxidizable fraction C_A, and the amount of hardly oxidizable ones is determined by equation 8. Both, the rate of intramolecular oxidation (ω %) and total nitrogen are determined in the same sample (Tab. 2). Fractionation is completed in 15 min.

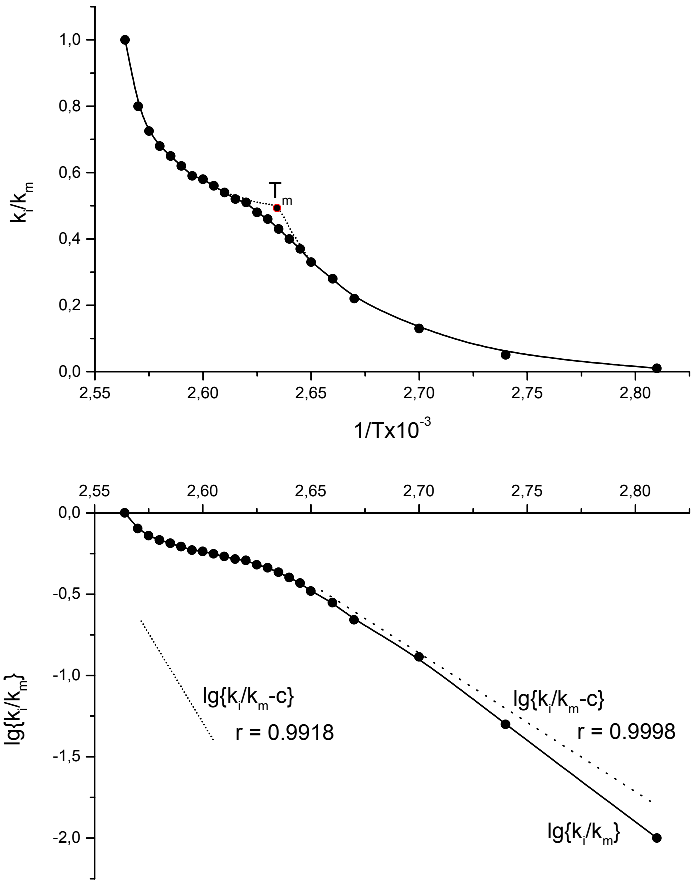


Fig. 2. *Relative change of the rate constant* (K_i / K_m) *with the temperature* $(-1/T^{10^{-3}})$ *during oxidative destruction of soil sample of Eutric Vertisol*

Table 2. Parameters of soil organic matter

SOIL TYPE (FAO, 1997)	C, %		T_M, ^{0}K	C_A, %	C_B, %	C_A/ C_B	C_f/C_h	C_h/C_f
	I	II						
Light Grey forest soil (Eutric Planosol)	0.990	1.090	381.68	0.81	0.18	4.5	4.2	0.24
Grey forest soil (Haplic Luvisol)	1.034	1.039	379.51	0.75	0.28	2.7	1.9	0.54
Leached Smolnitza (Eutric Vertisol)	1.880	1.750	380.37	1.13	0.75	1.5	0.3	3.26
Coal	38.40		380.37	10.3	28.08	0.4		

SOIL TYPE (FAO, 1997)	w, %	F	humus, %		N
			1.724	F	
Light Grey forest soil (Eutric Planosol)	-10.1	1.565	1.71	1.55	0.100* 0.096**
Grey forest soil (Haplic Luvisol)	-0.5	1.716	1.78	1.77	0.120 0.112
Leached Smolnitza (Eutric Vertisol)	+6.9	1.836	3.23	3.45	0.150 0.130
Coal					

*I - C content in studied sample, corresponding to CO_2 measured during destruction processes II - C content in studied sample, measured according CO_2,released as a result of reduction of oxidie agent excess *- nitrogen content (Kjelhdal method), measured in the equipment, after ending the destruction ** - nitrogen content (Kjelhdal method), measured after destruction (microchromatic method of Turin)*

$$F = \frac{172.414}{100 - W(\%)}$$

Determination of the rate of intramolecular oxidation (ω %) and total nitrogen of the fractions is carried out in the separate sample and destruction goes in a maximum temperature $T_{max}=380.37\ ^{o}K$. The process stopped when released CO_2 quantity corresponds to the amount of easily oxidizable fraction.

Soil samples of A horizons (sieved trough 0.25-mm openings) from Eutric Planosol, Haplic Luvisol and coal are analyzed as it is described above. The duration of the process is as follows: Eutric Planosol - 10 min., Haplic Luvisol - 9 min, and coal - 18 min. According to the ratio easily/hardly oxidizable fractions studied soils form the following order:

0.37 (coal) < 1.52 (Eutric Vertisol)< 2.66 (Haplic Luvisol) < 4.43 (Eutric Planosol)

Obtained similar results, reflected the changes of properties of genetic order, allow us to distinguish the structural components of humus substances in two fractions significantly differ in their stability - fraction A and B.

The investigation on kinetic of oxidazable thermodestruction shows that the progress of that process depends on the stability of the components corresponding to their structural features. The results obtained give a reason to define two hidhly differentiated humus fractions according to their thermal stability marked as A and B. Fraction A includes mainly organic compounds with aliphatic structure enriched in -OH, -COOH and other functional groups. These can be connected to the aromatic compounds as well. It is the most dynamic part of the humus and organic substances received into the soils. The humus substances of fulvic type enriched in -OH and -COOH groups as well as the organic substances which components are in the initial stage of humification are included in fraction A. Because of its instability and specific susceptibility to the changes in the environment this fraction gives a dynamic character of the properties of the colloidal soil formations. The degradation of fraction A needs relatively low energy.

"Srtuctural" determined fraction B is formated mainly by aromatic compounds and components of the humus compounds with maximal degree of aromaticity. If the conditions for their formation are changed, part of its components could be stabilised and the other part - disintegrate to more unstable components. The latest one gives the possibility to natural transfusion from one to another combination. Formation of organo - mineral compounds and the high oxidation state stabilises fraction B to biodegradation. This fraction is structural formation and stabilised colloid-chemical state of soil adsorbent. Their typical representatives are humin (unextractable carbon) and compounds that are in the composition of anthracite. More energy is needed to destroy fraction B.

The adequate of proposed fractional scheme is proved via similar results obtained, analysing samples applied methods mentioned above (Raytchev, 1992).

This type of grouping of components, build up the humus system is relative as many other attempts with the same purpose. For example from chemistry point of view unspecific organic compounds, hydrocarbons, polypeptides, acids, lipids, chlorophyll, pigments could be related to unstable ones, which content changes relatively fast. It could be expected that microorganisms consume them first and they serve as energy resource and nutritive reserve. Humic and fulvic acids, humates, lignin, polysaccharides are related to the more stable components towards microbial attach (Kononova, 1966; Orlov, 1985). Investigations with isolated humus substances have a number of conventions and possibilities for changes of native state of the components.

In this view on the investigations concerning status of humus system formation, as a component of soil adsorption complex, we aimed to present the significant role of stability and properties of soil colloid structures, which play in the manner of building. The part of individual organic compounds is subordinated. This ground correctness of the differentiated above and grouped of humus substances in two groups distinguished in their stability to oxidative destruction.

REFERENCES

Allison L. 1960**.** Wet combustion apparatus and procedure for organic and inorganic carbon in soil. *Soil Science Society of America***, 24, (**1), 36-40.

Charles M., M. Simmons. 1986. Analyst, 111, (4), 385.

FAO – UNESCO. 1997. Soil Map of the World. Revised Legend, ISRIC, Wageningen.

Filcheva E., L. Malinova. 1995. Comparative evaluation of methods for soil carbon determination. In: Proc. Jubilee Conference "70 years Forest education in Bulgaria", 7-9 VI 1995, Sofia, III, 19-25. (Bg)

Kononova M.M., 1966 Soil organic matter. It's nature, it's role in soil Formation and Soil Fertility. 2nd English Ed., Pergamon Press Inc., Elmsformd M.V., 544 pp.

Krastanov S., Konishev P., E. Filcheva, L. Petrova. 1986. On the method for calculating of humus in soil. Forest science, 6, 51-55 (Bg).

Methods for determination of humus content and composition. 1975. L., (Ru), 105.

Nikitin B. A. 1983. Particularization in method for humus determination in soil. Agrochemistry, 8, 101-106.

Nelson D. W., L.E. Somlers. 1982. Total carbon, organic carbon, amd organic matter. In: Methods for Soil Analysis, part 2. - Chemical and Microbiological Properties, 2nd ed. (Page A.L. R. H.Miller, R. Keemey eds., ASA-SSSA, Madison, WI, 539-580.

Orlov D. S., 1974. Soil humus substances. Univ. of Moscow Ed., Moscow, 333 pp. (Ru).

Orlov D. S. 1985. Soil chemistry. Univ. of Moscow Ed., Moscow, 376 pp. (Ru).

Orlov D. S., A. Tihomirov, Y. M. Ammsova 1985. Modern methods in investigations and characteristics of soil humus. Proceedings of Moscow University, 17, Soil Science, (1), 3-13 (Ru).

Raytchev, T., 1992. Method of fractionation of soil organic substance and of identifying structural components in the course of their oxidation destruction, Soil Science, Agrochemistry and Ecology, Sofia, vol. XXVII, 1: 22-27. (Bg).

Raytchev, T., 1996. Influence of organo-mineral interactions on colloid-chemical state of the soil adsorbent. D. Sci. Thesis, "N. Poushkarov" Inst., Sofia, 161 pp. (Bg).

Raytchev, T., P. Konishev, D. Donov. 1984. Application of thermal analysis in the studies on the structural evolution of humic substances. Soil Science and Agrochemistry, Sofia, 19, 4:82-87. (Bg).

Raytchev T., E. Filcheva. 1989. Method for simultaneously determination of humus and the rate of intermolecular oxidation of soil organic matter. Biological Science, 12, 101-103 (Ru).

Raytchev T., N. Mitsulov, E. Filcheva, I. Uzunov, P. Konishev, D. Lazarov. 1993a. Method and measuring system for determining content and the rate of intermolecular oxidation of soil organic matter. Invention certificate 46427/29.04, 1993, Sofia, Bulgaria. (Bg).

Raytchev T., N. Mitsulov, E. Filcheva, I. Uzunov. 1993b. Method and measuring system for determining of carbon content the rate of intermolecular oxidation of easily and hard oxidise fractions of soil organic matter. Invention certificate 47906/10.06.1993, Sofia, Bulgaria. (Bg).

Schnitzer M., S., U. Khan. 1972. Humic Substances in the Environmment., N. Y., Marcel Dekker E. R. VII, 327 pp.

Uzunov I. N. Mutsulov, T., Raichev, E. Filcheva, D. Lazarov, 1995. A measuring system for soil humus content determination. Oxidation Communication, 18, 4, 373-375

Uzunov I. 1993. Measuring system for determining soil humus content and fractionation in easily and hard oxidise fractions of soil organic matter. PhD. Thesis, Technical Univ., Sofia, 141 pp. (Bg).

Parameters and equations:

Initial data and measured parameters

T_o - temperature, maintained constantly in a thermostat, where a reaction vessel is put in

T_i - temperature in the reaction vessel in the moment τ_i

$\sum_{0}^{\tau_i} C$ - carbon content, oxidizes to CO_2 from the initial moment of oxidizable destruction to moment τ_i

C - total carbon content in the sample, determined by CO_2 amount released up to the moment when the destruction is over

Calculated parameters

1. $K_1 = \frac{1}{\tau_1} \ln \frac{C}{C - \sum_{0}^{\tau_i} c}$ - rate constant for reaction of first order

2. $K = K_o e^{-\frac{E}{RT}}$ - temperature dependent rate constant, where K_0- constant depending on inter energy of the substance; *E* - activated energy; *R* - Ridberg' constant.

3. $\frac{Ki}{Km} = 10^{\left(a - b \times \frac{1}{T_i}\right)}$ - relative change of rate constant with the changes of temperature in the reaction vessel, where K_m - maximum value of K_i *when* $T_i = T_m$.

$$a = \frac{1}{2.303} \frac{E}{R} \frac{1}{T_m} \qquad b = \frac{1}{2.303} \frac{E}{R}$$

Constants *a* and *b* are determined from data obtained by linear regression.

$$\log \frac{K_i}{K_m} = a - b \frac{1}{Ti}$$

4. $\frac{K_i}{K_m} = 10^{\left(a - b \times \frac{1}{T_i}\right)} + c$ where $c = \frac{y_1 y_2 - y_{\frac{2}{3}}}{y_1 + y_2 - 2 y_3}$

(x_1y_1) and (x_2y_2) - co-ordinates of two end points on the curve $\frac{K_i}{K_m} = f\left(\frac{1}{T_i}\right)$

y_3 *is* determined graphically on the base of mean geometrical $x_3 = \sqrt{x_1 x_2}$

5. $$\log\left(\frac{K_1}{K_m} - c\right) = a - b\frac{1}{T_i}$$

6. $\left(\frac{K_M}{K_m}\right)A = \left(\frac{K_M}{K_m}\right)B$ when $T_i=T_M$, where K_M - K_I value in point M, point of

interception for curves, presented graphically in co-ordinates $\frac{K_i}{K_m} = f\left(\frac{1}{Ti}\right)$

T_M - value of T_i in point *M; A* - index, related to easily oxidizable fraction; B- index, related to hardly oxidizable fraction;

7. $C_B = C - C_A$ carbon content in hardly oxidizable fraction, where C_A-carbon content of easily oxidizable fraction, determined of CO_2 released from the initial to the moment where $T_i=T_M$

DISTRIBUTION OF SURFACE CHARGE ON SOIL COLLOIDS

Raytchev T. [1]***, Jokova M.***[1]***,***
Jozefaciuk G.[2]***, Hajnos M.***[2]

[1] *N. Poushkarov Institute of Soil Science, 7 Shosse Bankja Str., 1080 P.O. Box 1369, Sofia, Bulgaria*
[2] *Institute of Agrophysics, Polish Academy of Sciences, 4 Doswiadczalna Str., P.O. Box 201, 20-209 Lublin, Poland*

Abstract

Studies on the relation between the colloid structure and density of the permanent and variable charge on the surface of soil colloid structure were carried out. Objects were two soils: Light grey pseudopodzolic forest soil (Eutric Planosol) and Leached smolnitza (Eutric Vertisol). The theory of the studies was based on the ideas about the three - layer structure of the soil colloids (organic, organo - mineral and mineral), predominating of the adsorption sites with acid character and high sensitivity of the negative charge to the changes in the structure porosity.

The experiment included destruction of the layers of the colloid structure by treatments of soil samples and the respective clay fractions (particle size < 2μm) by H_2O_2, $Na_4P_2O_7$, as well as by electrodialysis. After that the characteristics of adsorption ability and physicochemical properties of the obtained preparations were determined.

The amount of the permanent and variable charges and the ratio between them corresponded to the amount of the clay fractions and the types of the abundant clay minerals. The well pronounced negative charge of the mineral layer of the soil colloid structure caused an induction effect on the surface charge of bound with it adsorbing layers of the soil organic matter. This induction effect was more strongly expressed on the variable charge. They surface charge densities of the two layers were close, but they depended on the clay mineral type. The charge densities strongly decreased at the predominating of the montmorillonite group minerals, due to their higher surface in comparison with the kaolinite.

The bonds between the organic and organo - mineral layers was caused by cations - bridges, consisting of ionic forms of the polyvalent elements, mainly (Fe and Al), colloidal forms or their clathrate compounds. After treatment by H_2O_2 and separating of the outer layer the surface of the inner organo - mineral layer was appeared. That treatment destroyed these bridges, but it was not aggressive enough to brake the valence bonds between the humus acids and the slight acid exchanging sites of the soil clays and to release the variable charge on the octahedral surface.

An increase of the negative charge and the appearance of the well expressed capillary - condensation hysteresis after electrodialysis of the all studied samples could be related to the uncovered surface of a part of the clay minerals. The additional dispersion resulted in the higher increase of the variable charge, which was mainly ascribed to the ionised OH - groups on the slight acid octahedral surfaces. That effect was higher after the treatment by $H_2O_2 + Na_4P_2O_7$. The broken valence bonds between the humus substances and the clay minerals contributed to that effect. All treatments caused an increase of the middle radius of pores and of the distance between parallel planes of the layers. In A horizon of the Eutric Planosol the variable charge was the most strongly increased, which was due to the predominating of the kaolinite type clay minerals in the surface horizon of this soil. In the studied Eutric Vertisol the variable charges of the mineral layer was strongly blocked by the positively charged Fe and Al compounds or functional groups of humus acids. The differences in the genesis of the studied soils (in the current weathering and soil - forming processes) predetermined the predominating of kaolinite or montmorillonite clay minerals.

INTRODUCTION

The origin of adsorption sites differing in their ability on the adsorbing surfaces depends on the organisation of colloidal structures and the size and amounts of pores in them. The porosity of these structures influences the surface accessibility for the current adsorption processes.

Studies on the relation between the nature of the collide structures and density of the permanent and variable charge on their surfaces are required. Ideas about the three - layer structure (organic, organo - mineral and mineral) of the soil colloids, predominating of the adsorption sites with acid character and high variation of the negative charge with the changes in the structure porosity are the theoretical base of the carried studies (Raytchev and Matyka - Sarzynska, 2004; Raytchev and Benkova, 2004).

MATERIALS AND METHODS

The studies were carried out on the soil samples of three horizons of the following soils: Light grey pseudopodzolic forest, surface waterlogged and gleic, from Veltchevo village (region of Lovetch town) - A_1 (0 - 15 cm; B_2 (62 - 82 cm); C_1 (112 - 140 cm); Leached smolnitza, from Sredetz village (region of Stara Zagora town) - Ap (0 - 25 cm), B_1 (62 - 90 cm), C_1 (120 - 130 cm). (According to FAO classification – 1997, they are classified as Eutric Planosol and Eutric Vertisol, respectively)

Light grey pseudopodzolic forest soil, surface gleic, developed on acid parent materials (sands). It possesses well expressed textural differentiation in the distribution of clay particles along depth. The reaction changes from strongly acid (pH 4.5 at A horizon) to slightly acid (pH 5.7 at B horizon). The clay minerals in the surface horizon

(A_1) are mainly presented by chlorite (21%), micas (16%) and kaolinite (16%). High amounts of the free Si, Al and Fe (their sum was nearly 6%) and remarkable amounts of fine quartz (31%) were established (Atanasov, 1977; Atanasov and Dimitrov, 1976). In the illuvial horizon (B_2) the most predominating clay mineral was montmorillonite (37%), followed by micas (19%) and kaolinite (14%). In comparison with the surface horizon, in the B_2 horizon the amount of the fine quartz (13%) was lower, whereas the amount of the free forms were a little higher (their sum was nearly 7%) (Atanasov, 1977). In C_1 horizon the clay mineral composition and the free compounds content were similar, but the amount of montmorillonite was highest (44%).

Leached smolnitza soil, developed on old quaternary parent materials, was characterised by slight to middle clayey particle size distribution, without remarkable differences in the clay and silt content in the genetical horizons. The clay fraction was the predominating one. There were no changes in the trends of the clay mineral distribution along depth. Montmorillonite group dominated, followed by illit and kaolinite. Some amount of hydrogethite was found. The values of pH varied from 7.3 to 8.0.

An attempt was made to remove the particular layers of the colloid structure in the soil samples and their clay fractions (particle size < 2μm), extracted by the method of Aidinyan (1966). The treatments with H_2O_2 (Jackson, 1956); $Na_4P_2O_7$ and electrodialysis (Raytchev, 1997; Raytchev and Toncheva, 1997) were applied.

The specific surface (S_{BET}) of the untreated (initial) soil samples and treated ones was determined by the BET method, using the data of the low temperature adsorption of nitrogen vapour (Brunauer et al., 1938; Gregg and Sing, 1967). The surface of the transitional pores (Sp) and the volume of the micro - pores ($V\mu$) and of the transitional pores (Vp) were determined by the data of adsorption (Kiselev, 1949; Dubinin, 1966; 1970).

The amount of the permanent negative charge (T_{SA}) and variable negative charge (T_A) and their total sum ($T_{8.2}$), i. e. the amount of all exchangeable cations at pH 8.2 were determined by the method of Ganev (Ganev and Arsova, 1980).

RESULTS AND DISCUSSION

The obtained results of the absolute amount of the permanent and variable charge and the ratio between them in the studied soils and their clay fractions showed a good correspondence to the amounts of these fractions and the type of the clay minerals (Table 1). According to Ganev et al. (1990) in the acid soil (Light grey pseudopodzolic forest) that ratio is in the favour of the variable (pH dependent) charge, whereas in the slightly alkaline soil (Leached smolnitza) - the permanent (pH independent) charge dominates.

1. Studies on Light grey pseudopodzolic forest soil (Eutric Planosol).

1.1. Analysis of samples from A horizon.

Table 1. Adsorption and physicochemical characteristics of soil samples of Light grey pseudo-podzolic forest (Eutric Planosol, EP) and Leached smolnitza (Eutric Vertisol, EV)
1 - initial (untreated) sample; 2 - after treatment by H_2O_2; 3 - after electrodialyzis; S_{BET} - specific surface (Brunauer et al., 1938); S_p - the surface of the transitional pores (Kiselev, 1949); $T_{8.2}$ - the sum of the negative charge on the surface of the soil colloids, determined by the amount of exchangeable cations at pH 8.2 (Ganev and Arsova, 1980); T_{SA} - the amount of the permanent negative charge; T_A - the amount of the variable negative charge; $\sigma_0 = (T_{8.2}/S_{BET}).10^3$ cmol.m^{-2} - charge density; $\sigma_p = (T_{SA}/S_{BET}).10^3$ cmol.m^{-2} - the permanent charge density; $\sigma_v = (T_A/S_{BET}).10^3$ cmol.m^{-2} - the variable charge density.

Soil/Layer/sample			S_{BET}, m^2/g	S_p, m^2/g	Negative charges, cmol.kg^{-1}			Charge density, (cmol.m^{-2}).10^2			C, %
					$T_{8.2}$	T_{SA}	T_A	σ_o	σ_p	σ_v	
EP	A_1	1	21.2		9.2	3.9	5.3	43.4	18.4	25.0	1.38
		2	26.1		13.9	9.3	4.6	53.3	35.6	17.6	0.55
		3	30.5	12.3	14.7	6.8	7.9	48.2	22.3	25.9	1.64
	B_2	1	54.4	15.3	19.3	15.4	3.9	35.5	28.3	7.2	0.93
		2	60.9	15.8	18.9	15.7	3.2	31.0	25.8	5.2	0.51
		3	59.6	21.1	22.5	15.1	7.4	37.8	25.3	12.5	0.98
EV	A	1	82.3	21.3	27.8	25.1	2.7	33.8	30.5	3.3	1.95
		2	92.7	20.2	30.2	27.3	2.9	32.6	29.4	3.2	0.50
		3	98.4	22.8	31.4	28.5	2.9	31.9	29.0	2.9	2.17
	B_1	1	76.6	21.7	33.3	30.7	2.6	43.5	40.1	3.4	1.22
		2	77.5	18.4	32.8	30.0	2.8	42.3	38.7	3.6	0.59
		3	93.2	35.1	35.4	32.2	3.2	38.0	34.5	3.5	1.58

After the treatment by H_2O_2 of the untreated soil sample from A horizon new surfaces are uncovered, bearing the permanent charge. It is confirmed by the increase in S_{BET}, as well as in $T_{8.2}$ and T_{SA} (Table 1). There is no correspondence between the sharply increased surface density of these charges (σ_p) on the adsorption sites and the lower increase of their surface. The absence of the capillary - condensation hysteresis indicates that these surfaces possess the pores with high size (radius). The cavities are supposed to be blocked by the colloids of the hydroxides of the amphotheric elements and of some fragments of humus substances. The acid reaction of this soil allows the existence of the similar forms. Their separations during the treatment result in the overequivalent number of the counter - charged adsorption centres per unit surface.

The clay fraction treatment with H_2O_2 leads to the same trends of the changes, but they are less expressed than in the untreated sample (Table 2). The surface charge densities (σ_p and σ_v) are decreased, especially of the variable one. Maybe, the treatment by H_2O_2 is not aggressive enough to destroy the valence bonds between humus acids and slight acid exchanging sites on the clay surface and to release the variable charge. Probably, the cation - bridges between the two organo-mineral layers of "sandwich" structure are distracted, without affecting of the valence bonds.

Table 2. Adsorption and physicochemical characteristics of soil clay samples (particle size < 2μm) of Light grey pseudopodzolic forest (Eutric Planosol) and Leached smolnitza (Eutric Vertisol)
1 - initial (untreated) sample; 2 - after H_2O_2treatment; 3 - after electrodialyzis; 4 - after treatment by $H_2O_2 + Na_4P_2O_7$; S_{BET} - specific surface (Brunauer et al., 1938); Sp - the surface of the transitional pores (Kiselev, 1949); $T_{8.2}$ - the sum of the negative charge on the surface of the soil colloids, determined by the amount of exchangeable cations at pH 8.2 (Ganev and Arsova, 1980); T_{SA} - the amount of the permanent negative charge; T_A - the amount of the variable negative change; $\sigma_0 = (T_{8.2}/S_{BET}).10^3$ cmol.m^{-2} - charge density; $\sigma_p = (T_{SA}/S_{BET}).10^3$ cmol.m^{-2} - the permanent charge density; $\sigma_v = (T_A/S_{BET}).10^3$ cmol.m^{-2} - the variable charge density.

Soil/ Layer/Sample			S_{BET}, m^2/g	S_p, m^2/g	Negative charges, cmol.kg^{-1}			Charge density, (cmol.m^{-2}).10^2			C, %
					$T_{8.2}$	T_{SA}	T_A	σ_o	σ_p	σ_v	
E P	A_1	1	31.3		25.0	14.3	10.7	79.8	45.7	34.1	1.88
		2	36.6		27.0	16.1	10.9	73.8	44.0	29.8	0.74
		3	41.8		35.8	20.6	15.2	85.6	49.3	36.3	2.01
		4	42.2	38.0	55.2	34.2	21.0	130.8	81.0	49.8	0.23
	B_2	1	85.3	61.0	31.3	21.0	10.3	36.7	24.6	12.1	1.34
		2	86.3	40.0	32.9	21.8	11.1	38.1	25.3	12.9	0.59
		3	105.8	83.0	40.1	23.2	16.9	37.9	21.9	16.0	1.57
		4	134.1	78.0	64.7	43.2	21.5	48.2	32.2	16.0	0.24
E V	A	1	90.0	16.0	37.4	34.1	3.3	41.6	37.9	3.7	2.24
		2	118.4	24.0	40.5	36.1	4.4	34.2	34.4	4.9	0.68
		3	119.7	36.0	49.8	32.4	17.4	41.6	27.1	14.5	2.49
	B_1	1	94.5	10.0	40.4	36.9	3.5	42.8	39.0	3.8	1.75
		2	111.4	26.0	42.3	37.7	4.6	38.0	33.8	4.2	0.53
		3	129.3	49.0	46.5	32.9	13.6	36.0	25.4	10.6	1.94

The electrodialysis of the soil sample causes the higher increase of S_{BET} and of the amount of the surface charge in comparison with the treatment by H_2O_2, but the charge density is not influenced. The effect of the same treatment of the clay fraction on the changes of the surface negative charge is very well pronounced. The sharp increase of the variable charge amount suggests a brake in the valence bonds between the humus substances and clay minerals. The appearance of capillary - condensation hysteresis shows the presence of new pores with lower radii, which can be related to the partly uncovered clay mineral surface.

A result of additional treatment of clay fraction by $H_2O_2 + Na_4P_2O_7$ is the more complete uncovering of the mineral layer and nearly double increase of the surface charge of the both types - permanent and variable - and slight increase in the S_{BET} , which affects their density.

After all treatments an increase of the middle radius of the pores and of the distances between the parallel flat planes of the layers were observed. This effect is due to a release of organic matter from pore volume or to a dispersion effect of the electrodialysis and of $Na_4P_2O_7$. At all isotherms a slight capillary - condensation hysteresis of A type, typical of the cylindrical pores with uncovered ends or bottle - shape forms.

In the clay fraction of this sample amounts of kaolinite and fine dispersed primary minerals are highest. They contribute to the inner surface. The porosity is governed by cracks between contacting particles. The applied treatments strongly affect the dispersity of these particles. That changes the values of adsorption characteristics.

1.1. Analysis of samples from B_2 horizon.

The treatment by H_2O_2 of the untreated sample from B_2 horizon increases the volume of transitional pores, which results in the increase of the specific surface S_{BET}, without the influence on their surface (Sp) or uncovering of new surface charge. Their density on the total surface of that adsorbent is decreased. It can be assumed that the removed soil organic matter from the cavities is not bound through chemical bounds.

After the same treatment of the clay fraction, separated from the sample of B_2 horizon, the following changes are observed. The micro - pores volumes (V_μ) is increased, the volume of the transitional pores (V_p) and their surface (Sp) are decreased. The total surface (S_{BET}) and the charge density are not influenced. The amounts of the permanent and variable charge are slightly decreased.

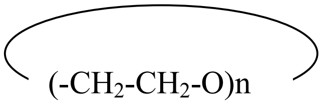
The results shown above suggest the following:

1. The treatment by H_2O_2 is aggressive enough to destroy the valence bonds between humus acids and soil clay. That would uncover significant amount of the variable charge on the surface of the uncovered volume of the transitional pores. But in this case such effect is not observed, since a high decrease of the value of V_p from 5.2 to 3.9 $(cm^3/g).10^2$ and slight increase of the value of V_μ from 1.9 to 2.8 $(cm^3/g).10^2$ are found. That is not typical of the soil clays, which are related to the adsorbents with heterogeneous transitional pores.

2. The treatment by H_2O_2 distracts the cation - bridges between humus substances and clay minerals. That would cause the increase in V_p and S_p, as well as the amount of the permanent charge T_{SA} (peculiar of the basal surfaces of the aluminosilicates). The experimental data are not convincing enough to prove that assumption.

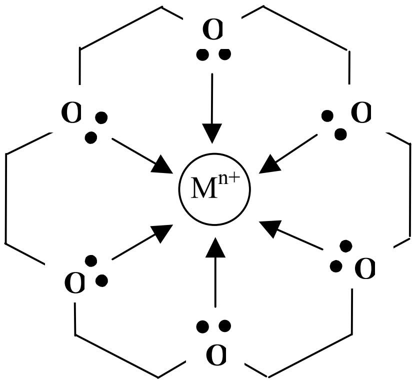
3. The treatment by H_2O_2 distracts the cation - bridges between the both organic layers of the colloid structures and after separation of the outer layer the surface of the inner organo - mineral layer is uncovered.

The bonds between the organic constituents of the two layers can be mainly formed through: ions, colloids and clathrate compounds of the amphotheric elements. The brake in the bonds with ions and colloids would be illustrated by high increase of the amount of the surface charge, which is not found in this case. The experimental data support the presence of bonds with clathrate compounds. Some of the substances are formed by the combination of one stable compound with other one or with atom or molecule, without any chemical bonds between the two components. These compounds crystallise as a form, possessing uncovered cavities, holes, and channels, in which the atoms or molecules of the other compound are kept. These compounds are clathrates (Cotton and Wilkinson, 1977a; 1977b). Most of them contain hydrogen bonds. A lot of clathrates possess the structure of honeycomb, which favours the including of other molecules in it. Such compounds are mainly cyclic polyesters with very good complex - formation ability (Petrov, 1996).Their molecules are formed like the rings of various numbers of ethylenoxy groups ($- CH_2 - CH_2 - O$). The cyclic polyesters can be expressed with the common formulae (n = 3 – 20):



$(-CH_2-CH_2-O)n$

The formation of the cyclic molecules, like the crown, called “crown - ethers” is due to the tetrahedric configuration of C atoms of the ethylene groups. Their complexes with metal ions are formed through bonds with the oxygen atoms in the cavities of the ring.



Probably, such compounds are also formed on the organo - mineral layer of the adsorbing structure. The organic matter is micro - porous adsorbent with low outer surface. The micro - pores are not accessible for the molecules, atoms and ions with relatively high size (particularly for nitrogen molecules). The peripheral parts of the humus molecules from the outer layers are more developed. They are rich in side - chains and functional groups, decreasing strongly the elasticity of their chains and limit the access to the belonging surfaces, especially in the inner organo - mineral layer (with exception of low temperature adsorption of nitrogen vapour). The different elasticity of the macromolecules from the two layers is a premise for the higher space after the aggregation. Probably, they are bound through clathrates, present in the cavities of the inner layer. After the separation of the outer layer of the clay sample through the treatment by H_2O_2 Sp is decreased. Maybe, the surface of the inner layer becomes smoother, confirmed by the decrease in the Vp and increase in V_μ.

The electrodialysis of the untreated sample contributes to the increase of S_{BET} - close to that after H_2O_2, and Sp - from 15.3 to 21.1 m^2/g. The total amount of the surface charge and the variable ones are increased, which density on the total surface is increased. An additional volume of the transitional pores is uncovered at the constant volume of the micro - pores. It confirms the suggestion that after the electrodialysis the part of the clay mineral surface is uncovered. The results correspond to the mineralogical composition of the soil at this depth of the profile. It is enriched in the montmorillonite minerals and with in pores with higher size. These trends (less expressed) are observed after the same treatment of the clay fraction.

The treatment by $H_2O_2 + Na_4P_2O_7$ of the untreated sample of B_2 horizon results in the much higher increase in S_{BET} and Sp and nearly double increase in the density of the permanent charge on the adsorbent surface. All that is related to the nearly complete uncovering of the mineral layer with higher surface and to higher distance between the parallel planes of the clay mineral layers than these in A horizon. The micro - porous space is also increased, probably due to the higher number of micro - pores in these layers. The deformations in the clay minerals favour the formation of enough cavities in the hexagon of the tetrahedic and octahedral layers, which are more accessible for the determination of their characteristics. This effect is higher after using of $H_2O_2 + Na_4P_2O_7$. The result of this treatment is the increase of the specific surface, especially at the montmorillonite predominating in the clays.

2. Studies on Leached smolnitza (Eutric Vertisol)

The changes in the adsorption ability and physicochemical characteristics after the same treatment of the samples from the two horizons of the Leached smolnitza are close to these observed in the B_2 horizon of the Eutric Planosol. It is due to the close amounts of clay fractions and predominating of the clay minerals from the montmorillonite group, but they amounts in the Eutric Vertisol is higher. It results in the increase of the values of: specific surface S_{BET}, permanent charge and density, surface of the transitional pores S_p. A strongly decrease of the variable charge is evident.

The obtained results after electrodialysis of the clay sample from A horizon show a higher increase (nearly 4 - fold) of the variable charge (T_A), than in the untreated clay sample, especially in the surface horizon. The surface charge of the variable charge σ_v is much increased. The organic matter content of this preparation is highest. This effect is clearer than in the first soil. Therefore, in the studied Eutric Vertisol the variable charge of the mineral layer (consisting mainly of montmorillonite) are more strongly blocked by the present free Fe, Al, and positively charged organic matter functional groups, especially in the surface horizon. In some Eutric Vertisols from Bulgaria the amounts of the variable (positive) charge and of the permanent (negative) ones are close. It is confirmed by the existence of ZPC (pH at which these charges are equivalent), determined for the surface horizons (Jokova, 2005).

The studied soils differ in the following. In the Eutric Planosol, developed on acid parent materials (sands), the destruction of the mineral lattices at high acidity and elluvial - illuvial distribution of the obtained products along depth have occurred. The surface horizon is poorer in clay fraction, in which kaolinite amount is higher. In the Eutric Vertisol, developed on old quaternary deposits, at slightly alkaline pH, the weathering process is less intensive than the formation of clay fraction, chacterized by the predominating of montmorillonite.

CONCLUSIONS

The results of the studies, included the destruction of the layers of the colloid structure through the treatment of the soil samples and the respective clay fractions (particle size < 2μm) by H_2O_2, $Na_4P_2O_7$, as well as electrodialysis, show the following. The amount of the permanent and variable charge and the ratio between them correspond to the amount of clay fractions and the type of the clay minerals.

The negative charge of the mineral layer of the colloid structure through induction effect influence the charges of the bound with it organic and organo - mineral layers. Probably this effect causes the well pronounced acid behaviour of the holle colloidal structure. The densities of the both permanent and variable charge are close, but in the presence of the montmorillonite (with higher surface than the kaolinite) these density is decreased.

The bonds between the organic and the organo - mineral layer of these structure are probably cation - bridges, the ionic and colloidal forms of the polyvalent elements (Fe, Al), as well as the clathrate compounds. The treatment by H_2O_2 destroys these bonds and after the separation of the outer layer the surface of the organo - mineral layer is uncovered. This treatment is not aggressive enough to breake the valence bonds between the humus acids and clay fractions and to release the variable charge on their surface.

The observed increase of negative charge and appearance of the well expressed capillary - condensation hysteresis after electrodialysis of all untreated and treated samples are related to the uncovering of the part of clay mineral surface. The additional dispersion reflects the more strongly increase of the variable charge, which originates mainly from the ionisation of OH - groups on the slight acid octahedral surfaces. The effect is better expressed after the treatment by $H_2O_2 + Na_4P_2O_7$ of the samples.

After the treatments of the clay samples from A horizon of the Eutric Planosol probably contributes to the brake in the valence bonds between humus substances and clay minerals. It is probably due to the predominating of the clay minerals of the kaolinite type in the surface horizon of this soil and acid soil reaction.

In the studied Eutric Vertisol the variable charges of the mineral layer is strongly blocked by the positive charged compounds of Fe, Al or functional groups of humus acids.

The differences in the genesis of the studied soils (in the current weathering and soil - forming processes) predetermine the amounts of kaolinite or montmorillonite clay minerals.

REFERENCES

Atanassov, Iv., 1977. Weathering and evolution of mineral part of the soils in Bulgaria. D. Sci. Thesis, Higher Agric. Inst., Sofia, p.566. (Bg)

Atanassov, Iv., D. N. Dimitrov, 1976. Distribution of the fine-dispersive minerals within the profile of light-grey gleyic soils. Soil Science and Agrochemistry, (XI) 3:17-25. (Bg)

Aydinyan, R. H., 1966. Accelerated method for extraction of soil clay and colloids using super-centrifuge. Agrochemistry, 6:151-156. (Ru)

Brunauer, S., P. H. Emmet, E. Teller, 1938. Adsorption of gases in multimolecular layers. Journal of American Chemical Society, 60, 309 – 314.

Cotton, A.F., G. Wilkinson, 1977a. Advansed inorganic chemistry. Part I. Science and Art Ed., Sofia. 677 pp. (Bg).

Cotton, A.F., G. Wilkinson, 1977b. Advansed inorganic chemistry. Part II. Science and Art Ed., Sofia. 756 pp. (Bg).

Dubinin, M. M., 1966. Modern State of Gaz and Vapor Adsorption by Microporous Solids, Ref. At the 20 the Congr. Of I.U.P.A.C., Butterworths, London.

Dubinin, M. M., 1970. Fundamental problems of the physical adsorption theory. Proc. I All-Union Conf. Theoretical Probl. Adsorption. Publ. “Nauka ”, M., p.476. (Ru)

Ganev, S., A. Arsova, 1980. Methods for determination of the strongly acidic and weakly acidic cation exchange in soils. Sofia, Soil Sci. and Agrochemistry,15 (3): 22-33 (Bg).

Ganev, St., A. Arsova, R. Sechkova, T. Kalichkova, A. Gateva, Chr. Tarpanova, 1990. Physico-chemical properties of the soils in Bulgaria an different regions of the World – a book of data. Agric. Academy and Soil Sci. Inst. N. Poushkarov – Soil Chemistry Dep., Sofia, p.54. (Bg)

Gregg, S. J., K. S. W. Sing, 1967. Adsorption, Surface Area and Porosity. Academic Press, London and New York.

Jackson, M. L., 1956. Soil Chemical analysis – Advance course: Published by the author, Univ. of Wisconsin, Madison, Wis

Jokova, M., 2005. Free forms of Fe, Al, Mn and ZPC of an Alisol and Vertisols. National Conference on Soil Science "Management, use and conservation of soil resaurces", 15 - 19 May, 2005. Sofia

Kiselev, A. V., 1949.Coll."Problems of kinetics and catalysis", M.-L., 6, 171. (Ru)

Petrov, G., 1996. Organic Chemistry, St. Kliment Ohridski University Press, Sofia, 703 pp. (Bg)

Raytchev, T., 1997. Kinetics of the desorption of cations. II. Desorption of exchangeable calcium depending on humus quality in the soil, Soil science, Agrochemistry and Ecology, Sofia, vol. XXXII, 4:37-39. (Bg).

Raytchev, T., R. Toncheva, 1997. Kinetics of the desorption of cations. I. A mathematical model testing, Soil science, Agrochemistry and Ecology, Sofia, vol. XXXII, 4:34-36. (Bg).

Raytchev T., D. Matyka-Sarzynska. 2004. Soil solid phase. In: "Physical Chemistry of soil surface and pore properties". Grzegorz Józefaciuk, Zofia Sokolowska, Mieczyslaw Hajnos (Eds.). Centre of Excellence for Applied Physics in Sustainable Agriculture Agrophysics, Institute of Agrophysics Polish Academy of Sciences, EU 5th Framework Program, QLAM-2001-00428, Lublin, 7-18.

Raytchev T., Benkova M., 2004. Organo-mineral complexes in soils and their interactions wiyh heavy metals. In: "Basic problems of Agrophysics". Dorota Matyka-Sarzynska and Ryszard Walczak (Eds.), Centre of Excellence for Applied Physics in Sustainable Agriculture Agrophysics, Institute of Agrophysics Polish Academy of Sciences, Lublin, pp.94-99.

ION-EXCANGE ABILITY OF SOIL ADSORBENT, KINETICS OF CATION DESORPTION

Raytchev T.[1]***, Toncheva R.***[1]***, Donov D.***[1]
Jozefaciuk G.[2]***, Sokolowska Z.***[2]

[1] *N. Poushkarov Institute of Soil Science, 7 Shosse Bankja Str., 1080 P.O. Box 1369, Sofia, Bulgaria*
[2] *Institute of Agrophysics, Polish Academy of Sciences, 4 Doswiadczalna Str., P.O. Box 201, 20-209 Lublin, Poland*

Abstract

The results of study of the influence of humic compounds on the ion-exchange propertis of the soil adsorbent and the mobility of cations included in its structure are presented. The investigations are done on organomineral samples from two clayey minerals (montmorillonite and kaolinite) and two soil varieties: Distric Planosol and Vertisol. The obtaining of the organo-mineral associates is based on a gradual saturation of the initial materials with newly formed humic substances in the process of decomposition of the chosen plant material.

The sorption capacity of the model samples is defined. The kinetic parameters are calculated after taking the desorption curves down by electrodialysis. The different influence of the humic substances on the sorption properties of clayey minerals from different type is shown. It is determined that after treatment with newly formed humic substances:

- The montmorillonite minerals slightly change their sorption ability of Ca;
- The kaolinite minerals strongly increase their sorption capacity.

Having in mind the above, the soil adsorbent of acid soils adsorbs significantly greater quantity of Ca after treatment with humic substances, while the change at Vertisol is insignificant.

The mobility of cations depends on their localization in the structure of soil adsorbent.

- The cations situated on the surface of its external organic layer and cations building the bridge bond between the external and the internal layer have close but weak stability as regarding to their electrochemical extraction;
- The cations connecting the primary organo-mineral kernel with the internel organic layer of the adsorbent and the cations building aggregative bridge bond be-

tween separate colloid units are comparatively more closely connected and are extracted by electro-dialysis with lower velocity;

- The cations included in the primary organo-mineral matrix are not extracted by electrochemical extraction.

Information about the connection between the evolution stage of the humic substances and the ion-exchange ability of the soil adsorbent is presented. It is supposed that the input of organic components in more advanced phase of humification will increase the stability of connection of calcium ions with the soil colloids.

INTRODUCTION

Position of different chemical forms of inorganic elements in the structure of the soil adsorbent defines their connection ability with the separate components and in general – the stability of the organo-mineral formation. In its structure are specified three different in their sensitivity to external influences fractions of humic substances:

- HS_{clay} – humic substances probably included in the primary organo-mineral matrix ($PM_{HS-clay}$)

The dehydrating effect of the presented polyvalent cations and the immediate phase contacts in absence of fluid layers add to these condensation structures considerable durability and non-reversibility at disintegration.

- HS_{int} – humic substances enriched with cyclic nuclear fragments included in the composition of the internal layer (L_{int}) connected directly with the organo-mineral PART ($PM_{HS-clay}$).

High elasticity of the organic polymolecular groups ensures denser phase contacts with the modified surfaces of clayey minerals. The presence of polyvalent cations facilitates the formation of comparatively shortened bridge bunches. Their stability increases at “klatrate“ location of these ions in conformation mobile chambers of the enriched with cyclic structures humic polymolecules which is not impossible because of their strongly expressed humic character.

- HS_{back} – humic substances from fulvic type connected with cation bridge bunch with the internal layer (L_{int}) which formed the external layer ($L_{back)}$ of the soil adsorbent (SA).

The availability of a great number of functional groups in their long chained molecules and the presence of polyvalent cations facilitates also the connection of the separate organo-mineral units in more compact aggregates by bridge mechanism of flocculation. May be assumed that this connection is more stable and its solidity is close to this of $L_{int} – PM_{HS-clay}$.

Chemical state of the inorganic elements defines largely the solidity of this connection. Their inclusion in organo-mineral associates decreases their mobility from the micelle areas, which in most of the cases are lower then the viability of the root system. This prevents their passing in the soil solution by desorption or as a result of the going solution processes within the vegetation period and define them as a potentially accessible for plants.

The aim of this study is to investigate the influence of the humic substances on the ion-exchange properties of the soil adsorbent and the mobility of cations included in its structure. The studies in this area in most of the cases are done on a preparative basis. This is made by a saturation of clayey minerals or by pure organic substances, or by fractions of humic compounds separated from different soils (Chassin et al, 1977; 1978; Greenland, 1971; Koyama, 1995; Schnitzer, 1969; 1991; Scnitzer and Kodama, 1966; Tarchitzky et al., 1993; Tisdall and Oades, 1982). In the last case, there is probability of a variation of the organic compounds under the influence of the chemical treatments and that makes the interpretation of the obtained results more complicated.

In this study, a different from the general approach is taken for obtaining the organomineral associations. It is based on the gradual saturation of clay with newly formed humic substances parallel to the decomposition of the chosen plant material.

MATERIALS AND METHODS

Objectives of the study are samples of two clayey minerals (montmorillonite and kaolinite) and two soils: Eutric Planosol from Veltchevo village and Eutric Vertisol from Sredetz. The sorption capacity of the model samples from the investigated objects is defined and after taking down the desorption curves by electro-dialysis are calculated the kinetic parameters.

The experimental models are obtained by the following way:

1. Organomineral associates obtained on the basis of Eutric Planosol saturated with humic substances and calcium cations as well as samples previously treated with H_2O_2. The choice of this object is based on the fact that on the acid soils is conducted a melioration with lime materials aiming the variation of acid-alkaline balance of the soil adsorbent.

EPI – initial soil;
EPI – OM – soil, saturated with humic substances;
EPI – Ca – OM – soil, consecutively saturated with Ca and humic substances;
EPI – Ca - soil, saturated with Ca;
EPI – Ca – OM – Ca –soil, saturated with Ca, humic substances (OM) and Ca again;
EPI – H_2O_2 –soil treated with hydrogenous peroxide;
EPI – H_2O_2 – OM –soil treated with hydrogenous peroxide and saturated with OM;
EPI – H_2O_2 – Ca – OM - soil treated with hydrogenous peroxide and saturated with Ca, OM and Ca again;
EPI – H_2O_2 – Ca –soil treated with hydrogenous peroxide and saturated with Ca;
EPI – H_2O_2 – Ca – OM –Ca –soil, treated with hydrogenous peroxide and saturated with Ca, OM and Ca again.

2. Organo-mineral preparation, obtained by Eutric Vertisol saturated with humic substances and calcium cations.

EV – initial soil;

EV – Ca – OM – Ca –soil, saturated with Ca, humic substances (OM) and Ca again.

3. Organo – clayey preparations, obtained by montmorillonite (Mt) and kaolinite (Kt) saturated with humic compounds and calcium cations.

Mt/Kt – initial minerals;

Mt/Kt – Ca – OM – Ca – clayey minerals saturated with Ca, OM and Ca again.

4. Monoionic organoclayey preparations obtained by montmorillonite (Mt) saturated with humic compounds, Ca, Mg, K and Na.

Mt – Ca – OM, Mt – Mg – OM, Mt – K – OM and Mt – Na – OM;

Mt – Mg – OM – Mg, Mt – K – OM – K and Mt – Na – OM – Na.

The experimental models are obtained by the following way:

On 10 g of the analyzed clay (montmorillonite – Mt or kaolinite – Kt) or the soil sample (EPI or EV) preliminary treated with 1n $CaCl_2$ (by montmorillonite – and with $MgCl_2$, KCl or NaCl) are added 10 g plant material which is poured with 100 ml distil water. The compostation is done in especially adapted pots in which is achieved the separation of two solid phases. The process is going at 25^0C for 60 days. After that the organo – mineral suspensis is centrifuged and the precipitate is washed with a distil water until all chlorine ions dissappear. The rest is dried at 40^0C. A part of the samples are additionally saturated with Ca (and montmorillonite – also with Mg, K or Na) for creating monoionic models.

The organic carbon is determined by wet burning through Tjurin's method (Kononova, 1966) and sorption parameters – through St. Ganev's method (Ganev & Arsova, 1980).

It may be expected that the way of connection between mineral and organic soil colloids as well as the type of exchangeable cations strongly influence the sorption capacity and the mobility of the adsorbed ions in newly formed organomineral associates (Stevenson, 1982; Schnitzer, 1969; 1991; Koyama, 1995; Orlov, 1985). It may be assumed that the desorption rate of exchangeable cations from organo-omineral compounds will distinguish essentially from their desorption rate of the corresponding mineral colloids.

The investigation of kinetics of the desorption of Ca cations is done through the observation of the extracted rate changes by electro-dialysis of suspensions of the model preparation in 0,3n H_3BO_3 in three-chamber electro-dialyzer at the following work regime: constant values of tension (250 V); gradient of the potential of the field (50 V/cm) and through cellophane membranes. Every 60 minutes the composition and the quantity of the cations in the extract and the corresponding kinetic parameters (the quantity of the extracted fraction Q, the rate constant k and the time of semi-decomposition $t^{1/2}$) are determined. Their calculation is done by the kinetic equation for second order reaction by a specially developed mathematical model.

MATHEMATICAL MODEL

The previous investigations on the extraction of exchangeable Ca by electrodialysis of the soil suspensions show that all desorption curves have well expressed parabolic direction. The availability of a "bend" at using the linear form is established. For that reason the desorption curves are composed from two parts which characterized the cation extraction related to different power respectively in different way in colloid system.

The investigation of the order of the reaction through the first, second and third order kinetic equations determined that the obtained curves are best described with the reaction equation of second order which linear form is:

$$\frac{\tau}{\mathbf{q}} = \frac{1}{\mathbf{k}} \times \frac{1}{\mathbf{Q}^2} + \frac{1}{\mathbf{Q}} \times \tau \qquad (1)$$

where:

q –quantity of extracted cations (cmol.kg^{-1}) for a period τ (min);

Q –maximal quantity of cations in the sample (cmol.kg^{-1});

K –rate constant of the second order reaction.

The constants $\frac{1}{k \times Q^2}$ and $\frac{1}{Q}$ in the equation (1) are calculated through linear regression.

The extraction curve q = F(τ) and the corresponding lines, described by $\frac{\tau}{Q} = f(\tau)$ are shown in Fig. 1.

In most of the cases, two rectilinear sections forming an angle are observed in their running. The appearance of the "bend" is a result of a change of the extraction rate and is an indication of availability of adsorption centers with different activity regarding the investigated cations. It may be assumed that until appearance of the "bend" two reactions undergo in parallel. After the depletion of cations extracted with a higher rate (higher values of k) continues the extraction only of the more strongly connected cations (lower values of k). Hence after period τ_n corresponding to intersection of the two curves the increase of the total quantity of cations in the extracts is at the expense of the extracted with lower rate only. This allows the determination of their quantity and the rate constant of the slower reaction. For this purpose are used experimental date after τ_n (τ_n is conditionally accepted for the slower reaction).

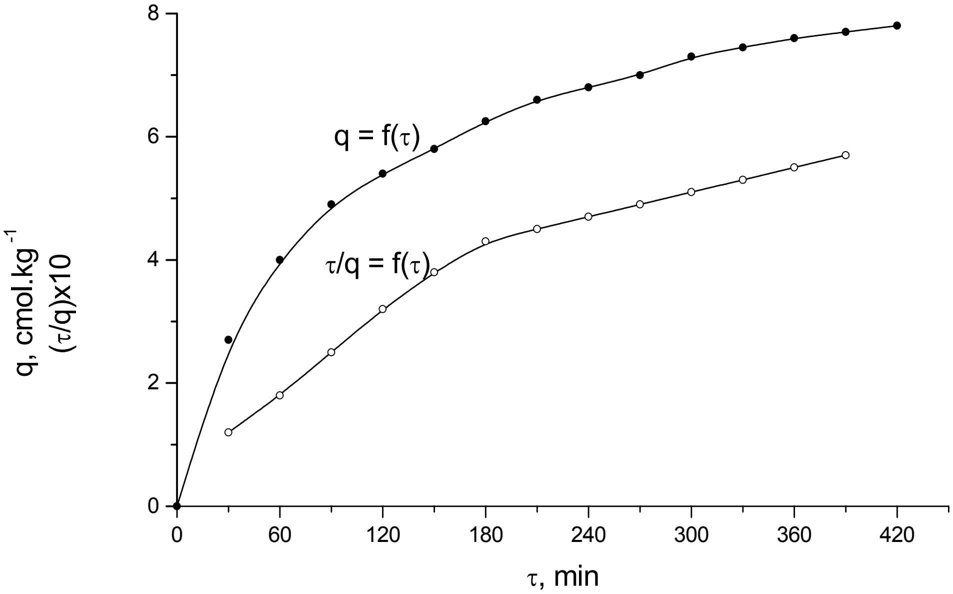


Fig. 1. *Kinetics of desorption of the exchangeable Ca-forms from soil sample by electrodialysis*

Practically this is done by constructing systems of equations. These systems describe the running of relation $\frac{\tau}{Q} = f(\tau)$ at $\tau < \tau_n$

$$\frac{\tau}{q} = \frac{1}{k^I} x \frac{1}{Q^{I2}} + \frac{1}{Q^I} . \tau \qquad (2)$$

and for $\tau > \tau_n$

$$\frac{\tau}{q} = \frac{1}{k^{II}} x \frac{1}{Q^{II2}} + \frac{1}{Q^{II}} . \tau \qquad (3)$$

The constants

$$A^I = \frac{1}{k^I} x \frac{1}{Q^{I2}}; \; B^I = \frac{1}{Q^I} \qquad \text{and} \qquad A^{II} = \frac{1}{k^{II}} x \frac{1}{Q^{II2}}; \; B^{II} = \frac{1}{Q^{II}}$$

are calculated by linear regression. The precision of the determination increases with the dropping of experimental data, which are found just next to τ_n.

It is experimentally determined that maximal cation quantity (Q), which would be extracted under infinite process, corresponds to the calculated value of Q^{II}. The rate constant of the reaction at which the extraction of cations is done with lower rate is: $k^{II} = k_2$ and $Q^{II} = Q$. At the intersection of two lines (at $\tau=\tau_n$) we have $A^I+B^I.\tau_n = A^{II}+B^{II}.\tau_n$ and hence:

$$\tau_n = \frac{A^{II} - A^{I}}{B^{I} - B^{II}} \tag{4}$$

and extracted quantity of cations before $\tau=\tau_n$ is

$$Q_n = \frac{\tau_n}{A^I + B^I \tau_n} = \frac{\tau_n}{A^{II} + B^{II} \tau_n} \tag{5}$$

Until $\tau \leq \tau_n$ two reactions run parallel and after $\tau \geq \tau_n$ only one continues or schematically

$$\begin{array}{l} Q \xrightarrow{k_1} Q_1 \\ \underset{\tau_n}{\overline{\qquad\qquad}} \xrightarrow[k_2]{} Q_2 \end{array}$$

. At the initial moment $\tau=0$ $[Q_0] = Q$, and $[Q_1]_0 = [Q_2]_0 = 0$ and at the moment τ of the beginning of the process the concentrations are

$$[Q]_\tau = [Q - q_1 - q_2],\ [Q_1]_\tau = q_1 \text{ and } [Q_2]_\tau = q_2$$

Then the rate of the first reaction is

$$V_1 = \frac{dq_1}{d\tau} = k_1 \times (Q - q_1 - q_2)^2 \tag{6}$$

and of the second reaction is

$$V_2 = \frac{dq_2}{d\tau} = k_2 \times (Q - q_1 - q_2)^2 \tag{7}$$

Hence $\frac{V_1}{V_2} = \frac{dq_1}{dq_2} = \frac{k_1}{k_2}$ or $q_1 = \frac{k_1}{k_2} \times q_2 + const$. But at $\tau=0$, $q_1=q_2=0$ and const=0. Hence

$$q_1 = \frac{k_1}{k_2} \times q_2 \tag{8}$$

After substituting (8) in (6):

$$\frac{dq_1}{d\tau} = k_1(Q - q_1 - q_2 \times \frac{k_2}{k_1})^2 = k_1(Q - \frac{k_1 + k_2}{k_1} \times q_1)^2 \qquad (9)$$

At $b_1 = \frac{k_1 + k_2}{k_1}$,

$$\int \frac{dq1}{(Q - b1 \times q1)2} = k1 \int d\tau$$

or $\frac{1}{b_1 \times (Q - b_1 \times q_1)} = k_1 \times \tau + const$

But since at τ = 0, $q_1 = q_2 = 0$, then $const = \frac{1}{b_1 \times Q}$ and

$$\frac{1}{b_1 \times (Q - b_1 \times q_1)} = k_1 \times \tau + \frac{1}{b_1 \times Q}$$

from where follows that

$$q_1 = \frac{k_1 \times Q^2 \times \tau}{1 + (k_1 + k_2) \times Q \times \tau} = \frac{k_1 \times Q_1^2 \times \tau}{1 + k_1 \times Q_1 \times \tau} \qquad (10)$$

Until $\tau = \tau_n$ the quantity of extracted with lower rate cations is

$$q_{2n} = \frac{k_2 \times Q^2 \times \tau_n}{1 + k^I \times Q \times \tau_n} = \frac{k_2 \times Q_2^2 \times \tau_n}{1 + k_2 \times Q_2 \times \tau_n}$$

The decision of the upper equation regarding the unknown leads to the quadratic equation $ax^2 + bx + c = 0$ where

$x=Q_2$
$a = 1 + k^I \text{ x } Q \text{ x } \tau_n$
$b = -Q^2 \text{ x } k_2 \text{ x } \tau_n$
$c = -Q^2$, which roots are $x_{1,2} = \frac{-b \pm \sqrt{b^2 - 4 \times a \times c}}{2a}$

But $Q_2 \geq 0$ and hence

$$Q_2 = \frac{Q^2 \times k_2 \times \tau_n + \sqrt{(Q^2 \times k_2 \times \tau_n)^2 + 4 \times (1 + k^{1} \times Q \times \tau_n) \times Q^2}}{2 + (1 + k \times Q \times \tau_n)} \qquad (11)$$

Then

$$q_{2n} = \frac{k_2 \times Q_2^2 \times \tau_n}{1 + k_2 \times Q_2 \times \tau_n} \qquad (12)$$

$$Q_1 = Q_n - q_{2n} \qquad (13)$$

The quantity of extracted with lower rate cations is calculated by the formula

$$q_2 = \frac{k_2 \times Q_2^2 \times \tau}{1 + k_2 \times Q_2 \times \tau} \qquad (14)$$

and since $q_1 + q_2 = q$, then $q_1 = q - q_2$ (15) until $q_1 \leq Q_1$.

The curve character $\tau/q = f(\tau)$ is rectilinear and this allows the calculation of the rate constant k_1 of the reaction in which cations with highter rate are extracted .

The method of calculation is illustrated by the following example:

τ(min)	q(cmol.kg^{-1})	τ/q
0	0,0	-
60	4,06	14,78
120	5,02	23,90
180	5,58	32,24
240	6,08	39,47
300	6,41	46,80
360	6,69	53,81
420	6,93	60,61
480	7,13	67,32

The two straight lines (Fig. 1.) drawn through the experimentally obtained values for $\tau/q = f(\tau)$ are intersected between the third and fourth points (180 – 240 min). The kinetic parameters calculated for ionic extraction for two lines separately are the following:

- For the first three points (to 180min inclusive)

$$A^{I} = \frac{1}{k^{I} \times Q^{I2}} = 6{,}18 \qquad B^{I} = \frac{1}{Q^{I}} = 0{,}146$$

m = 3 $Q^{I} = 6{,}85$ F = 1503,2

$k^{I} = 3{,}45 \text{ x } 10^{-3}$ r = 0,9997

- For the last four points (from 300 to 480 min inclusive)

$$A^{II} = \frac{1}{k^{II} \times Q^{II2}} = 12{,}70 \qquad B^{II} = \frac{1}{Q^{II}} = 0{,}114$$

m = 4 $Q^{II} = 8{,}77$ F = 20138,5
$k^{II} = 1{,}02 \text{ x } 10^{-3}$ r = 0,9999

The extracted ionic quantity ($Q_{\mathbf{n}}$) to intersection for time $\tau_{\mathbf{n}}$ is calculated by the equations (4) and (5).

$\tau_n = 203{,}8$ $Q_n = 5{,}67$

Until $\tau_n \leq 203{,}8$ the theoretical values of τ/q and q are calculated by means of A^{I} and B^{I}, and when $\tau_n > 203{,}8$ - by A^{II} and B^{II} to $\tau_n = 480$min.

At $\tau = \tau_n = 203{,}8$ Q_2 is calculated by equation (11)
$Q_2 = 5{,}32$
According to (12) $q_{2n} = 2{,}23$ and hence
$Q_1 = Q_n - q_{2n} = 3{,}44$
Then $Q = Q_1 + Q_2 = 8{,}76$.

To find the corrected value of Q_1 by the equations (14) and (15) the values of q_1 and q_2 are calculated. Through the linear regression the kinetic equations for the first reaction are determined:

$Q_{1corr} = 4$ $K_1 = 8{,}97 \times 10^{-3} \tau_{1/2} = 184{,}3$

The sum of the exchangeable ions extracted from the tested model is
$Q = Q_{1corr} + Q_2 = 4 + 5{,}32 = 9{,}32 \text{ cmol.kg}^{-1}$.

The final results are presented by the following:

Kind of the sample	Q_1 (cmol.kg^{-1})	K_1	$\tau_{1/2}$	Q_2 (cmol.kg^{-1})	K_2	$\tau_{1/2}$	$\sum Q$
Soil	4	$8{,}97 \times 10^{-3}$	27,9	5,32	$1{,}02 \times 10^{-3}$	184,3	9,32

RESULTS AND DISSCUTION

Sorption capacity of the organomineral samples with montmorillonite

The saturation of the initial montmorillonite (Mt – Ca or Mt – K) with humic compounds (OM) causes a decrease of the sorption capacity (Table 1) of the newly formed complex (Mt – Ca – OM and Mt – K – OM). This action is mainly reduced to blocking of the adsorption centers on the strongly acid ion-exchanger ($T_{CA}>>T_A$). It may be supposed that at the aggregation of mineral fractions in organomineral associates is a part of the permanent charges is blocked on their surfaces. But the different degree of the decrease of the sorption capacity depending on the cation type shows that other factors are also involved. The reasons are in the blocked action of the adsorbed organic compounds as well as in the different action of calcium and potassium ions on the crystalline lattice of montmorillonite.

Table1. Sorption capacity of different ionic forms of montmorillonite (Mt) and their associates with humus

Samples	$T_{8.2}$	T_A	T_{SA}	T_A	T_{SA}
	cmol kg^{-1}			% from $T_{8.2}$	
Mt-Ca	102.2	2.6	99.6	2.5	97.5
Mt-Ca-OM-Ca, hum	91.6	3.0	88.6	3.2	96.8
Mt-Ca-OM, hum	87.4	2.2	85.2	2.5	97.5
Mt-К	96.6	4.1	92.5	4.2	95.8
Mt-К-OM-К, hum	81.5	4.8	76.7	5.9	94.1
Mt-K-OM, hum	79.9	3.4	76.5	4.3	95.7
Mt-Mg	99.6	6.2	93.4	6.2	93.8
Mt-Mg-OM-Mg, hum	88.9	6.1	82.8	6.9	93.1
Mt-Mg-OM, hum	87.7	5.3	81.4	6.1	93.9
Mt-Na	101.1	7.1	94.0	7.0	93.0
Mt-Na-OM-Na, hum	85.3	9.7	75.6	11.4	88.6
Mt-Na-OM, hum	82.7	6.9	75.8	8.3	91.7

OM – samples treated with humic compounds by saturation with humus extracts; Hum – during humification process. $T_{8.2}$ – The sum of the negative charge on the surface of the colloids determined by the amount of exchangeable cations at pH 8.2 – total cation exchange capacity (CEC) (Ganev and Arsova, 1980): T_{SA} – the amount of the permanent negative charge – CEC of strongly acidic exchange complex; T_A – the amount of the variable negative charge - CEC of weakly acidic exchange complex. The sequence of the symbols corresponds to the respective treatment.

The availability or the additional input of Ca in the organomineral complex does not influence directly blocking of the adsorption centers of basal surfaces. Its influence is expressed in the area decrease of mineral grains as a result of the strong aggregative ability of the generated calcium humates.

The action of potassium ions is a little bit more complicated:

- The preliminary saturation of the initial montmorillonite with K may cause shrink of the inter-packed spaces of the crystalline lattice. This may hamper the adsorption of the basal surfaces;
- The preliminary saturation of the montmorillonite with humic substances would diminish the action of the potassium ions because of the embarrassed access to the inter-packed spaces and the additional treatment with potassium salt may cause an extreme change in the crystalline lattice;
- At the treatment of the organomineral montmorillonite associate with KCl potassium humates may be generated. They do not have so well expressed aggregated effect on the mineral parts in comparison with more difficult mobile humates of calcium and this will not decrease the associate area essentially;

Hence, the treatment with K may cause the accumulation of some inter-directed effects, which complicates the interpretation of the results.Also important is the way in which organomineral associates are obtained. In the conditions of the plant material humification, the montmorillonite is previously treated with definite type of cations. The course of compost is long (60 days). Besides the running the synthesis on the higher molecular level organic combinations on the mineral is possible. The aggressive influence of the organic complex-formed ligands is a precondition for more effective blocking of the basal surfaces with respect to exchangeable cation access.

Most considerable decrease of the sorption capacity of the basal surfaces is observed at sodium- and potassium-saturated models and little less – at these saturated with magnesium. By level of influence on this decrease the exchangeable cations formed the row:

Na > K > Mg > Ca

Their influence on the raised values of the sorption capacity of the light acid ion-exchanger is the following:

Na > Mg > K > Ca.

The fact that the investigation is done on the monoionic organomineral preparations obtained by newly formed humic substances have to be considered.

Kinetics of cation desorption

The developed mathematical method for processing the experimental data is applied to study the influence of the humic compounds on the kinetics of calcium desorption from the model preparations. They are obtained by Distric Planosol samples. The observed changes of the determined values of their kinetic parameters can be summarized in Table 2.

Table 2. Kinetic parameters of Distric Planosol (DPl) and of their associates with Ca and humus

Sample	∑ Ca	Ca_1	Ca_2	K_1, min^{-1}	$\tau^{1/2}$, min.	K_2, min^{-1}	$\tau^{1/2}$, min.
	cmol.kg^{-1}						
DPl	1.6	1.6		$3.6x10^{-2}$	17.5		
DPl-OM, hum	6.4	3.0	3.4	$8.2x10^{-3}$	13.7	$3.7x10^{-3}$	79.3
DPl-Ca-OM, hum	8.8	4.3	4.5	$5.3x10^{-3}$	27.9	$1.8x10^{-3}$	126.1
DPl-Ca	9.3	4.0	5.3	$3.4x10^{-3}$	16.6	$1.0x10^{-3}$	184.3
DPl-Ca-OM-Ca, hum	24.3	14.6	9.7	$2.5x10^{-3}$	14.2	$5.2x10^{-4}$	197.8
DPl-H_2O_2	2.4	2.4		$3.0x10^{-2}$	13.2		
DPl-H_2O_2-OM, hum	3.7	3.7		$2.0x10^{-2}$	17.1		
DPl-H_2O_2-Ca-OM, hum	6.5	6.5		$9.0x10^{-3}$	42.9		
DPl-H_2O_2-Ca	9.0	9.0		$2.6x10^{-3}$	17.2		
DPl-H_2O_2-Ca-OM-Ca,hum	11.9	11.9		$4.9x10^{-3}$			

OM – samples treated with humic compounds: Hum – during humification process. H_2O_2 - sample treated with H_2O_2; Ca - sample after treatment by $CaCl_2$. The sequence of the symbols corresponds to the respective treatment.

This table was constructed in the following way:

1. Initial soil – a fraction of little quantity slightly connected Ca – K_I=3,6.10^{-2}.
2. Initial soil + OM (DPI - OM) – 4 times more Ca in comparison with DPI;

- Two fractions – the second fraction is more strongly connected: K_{2OM}/K_{1OM}=4,5.10^{-1};
- The first fraction is more strongly connected in comparison with the initial soil fraction: K_{1OM}/K_I=2,2.10^{-1}.

3. Initial soil + Ca (DPI – Ca) – 5,8 times more Ca in comparison with DPI and 1,4 times more Ca in comparison with DPI – OM;

- Two fractions – the second fraction is more strongly connected: K_{2Ca}/K_{1Ca}=3.10^{-1};
- The first fraction is more strongly connected in comparison with the fraction of the initial soil: K_{1Ca}/K_I=9,0.10^{-1};
- The second fraction is strongly connected in comparison with its analogous fraction from DPI – OM: K_{2Ca}/K_{2OM}=2,7.10^{-7};

4. Initial soil + Ca + OM (DPI – Ca – OM) – 5,5 times more in comparison with DPI, a quantity almost equal to that of DPI – Ca and corresponding to that – 1,4 times more Ca in comparison with DPI – OM;

- Two fractions – the second fraction is more strongly connected: K_{2CaOM}/K_{1CaOM}=3,4.10^{-1};

- The first fraction is more closely connected in comparison with the fraction of the initial soil: $K_{1CaOM}/K_1=1,5.10^{-1}$;
- The second fraction is strongly connected in comparison with its analogous fraction of DPI – OM: $K_{2CaOM}/ K_{2OM}=4,9.10^{-1}$;

5. Initial soil + Ca + OM + Ca (DPI – Ca –OM – Ca) – 15 times more Ca in comparison with DPI and 2,6 times more in comparison with DPI – Ca;

- Two fractions – the second fraction is more strongly connected: $K_{2CaOMCa}/ K_{1CaOMCa}=2.10^{-1}$;
- The first fraction is more strongly connected in comparison with the fraction from the initial soil: $K_{1CaOMCa}/K_1=7.10^{-1}$;
- The second fraction is twice more and is with approximately an order more strongly connected in comparison with its analogous fraction from the other models: $Ca_2=9,7$ cmol.kg^{-1} and $K_{2CaOMCa}=5,2.10^{-4}$.

The structure-adsorption investigations on the sensibility of SA to different treatments show that the electrodialysis is sufficiently aggressive for the bunch destructions between its three layers without affecting the primary organomineral kernel. The reason for the appearance of two different by connection solidity with the soil adsorbent calcium fractions can be found in its different local presence (fig.2).

- on the surface of the external organic layer (L_{back});
- between the internal (L_{int}) and the external (L_{back}) layer;
- between the internal layer (L_{int}) and primary organomineral kernel ($PM_{HS-clay}$);
- between aggregate colloid units.

It can be supposed that the last two positions insure higher stability of the connection taking into consideration its shorting and difficult access to the cation bridges.

The lack of two calcium fractions in the initial soil (EPI) is possibly connected to physic-chemical condition of its colloid ionic exchanger. The quantity of the available calcium is small, the kaollinite is a leading clayey mineral, the humus is of fulvate type, the aggregation is low and the connection with the components of soil adsorbent is too slight. With the increase of the calcium quantity (sample EPI – Ca) the aggregation of the parts also increases. The available organic substances from the external layer of soil adsorbent take a part in the process of their flocculation. A part of calcium, which takes a part in this process, is included in its more strongly connected fraction (Fig.2).

In the running of saturation of the initial sample with humic compounds (EPI OM), the result is similar to those of the model EPI – Ca with the different that the quantity of Ca is lower and the aggregative effectiveness is slighter. The increased quantity of humus at the account of its newly formed components does not modify essentially the established kinetic parameters. It can be supposed that its low degree of humification is a reason for the slight cation connection between him and the soil adsorbent (SA) of the tested soil.

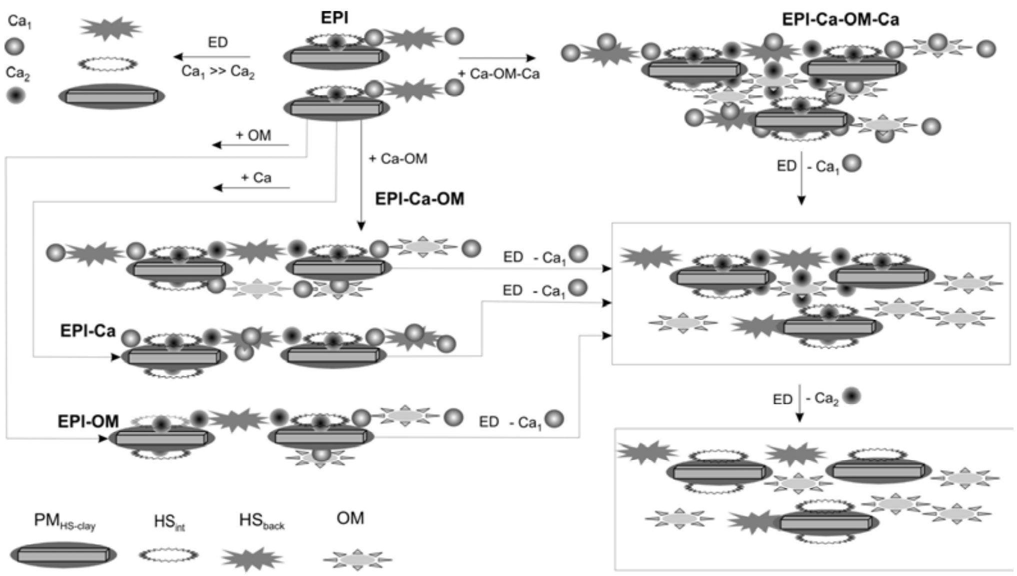


Fig. 2. *Change of structure of soil adsorbent (SA) of Eutric Planosol (EPl) after treatment for calcium and humus substance and after desorption the exchangeable Ca-forms from soil samples by electrodialysis*

PM$_{HS\text{-}clay}$ – primary organo-mineral matrix of SA; HS$_{int.}$ – humus substance from interaction layer of Soil adsorbent; HS$_{back}$ - humus substance from back layer of SA; OM – neoplasme of humus substance during humification process of oak leaves. The sequence of the symbols corresponds to the respective treatment.

The kinetic parameters of the model EPI – Ca – OM do not distinguish significantly these of the models EPI – Ca and EPI – OM. That result confirms the assumption for slight influence of newly formed humic substances (OM) on the connection solidity of calcium in SA. A proof of that are the changes of the models obtained after processing the initial soil with H_2O_2. A second fraction of Ca is absent at all organomineral samples of this series irrespective of the increase of its quantity (Table 3).

With the quantity increase of the input calcium jointly with newly formed humic substances (EPI – Ca – OM – Ca) the values of its kinetic parameters are sharply modified. There is a significant increase of the two fractions Ca in comparison with all investigated models. At the same time their connection with the active centers of SA is retrieved. A probable reason for that is the created too complicate pore system between the formed aggregate. This is done also with the participation of newly formed humus (fig.2). The inclusion of Ca in these strongly negative interaggregate spaces hampers its extraction. This reflects negatively on the extraction rate.

Table 3. Sorption capacity of calcium forms forms of montmorillonite (Mt), kaolinite (Kt) and studied soils (Distric Planosol-DPl and Vertisol – V) and of their associates with humus

Sample	$T_{8.2}$	T_A	T_{SA}	T_A	T_{SA}	C %
	cmol.kg^{-1}			% from $T_{8.2}$		
Mt-Ca	102.2	2.6	99.6	2.5	97.5	0.17
Mt-Ca-OM-Ca, hum	91.6	3.0	88.6	3.2	96.8	0.77
V	40.4	3.5	36.9	8.7	92.3	1.75
V-Ca-OM-Ca, hum	38.7	7.2	31.5	18.6	81.4	1.95
Kt-Ca	6.6	0.9	5.7	14.5	85.5	0.15
Kt-Ca-OM-Ca, hum	9.0	2.2	6.8	24.4	75.6	0.55
DPl	25.0	10.7	14.7	42.8	57.2	1.88
DPl-Ca	24.6	10.4	14.2	42.3	57.7	1.79
DPl-Ca-OM-Ca, hum	34.6	7.1	27.5	20.5	79.5	2.51

OM – samples treated with humic compounds: Hum – during humification process.
$T_{8.2}$ – The sum of the negative charge on the surface of the colloids, determined by the amount of exchangeable cations at pH 8.2 – total cation exchange capacity (CEC) (Ganev and Arsova, 1980): T_{SA} – the amount of the permanent negative charge – CEC of strongly acidic exchange complex; T_A – the amount of the variable negative charge - CEC of weakly acidic exchange complex.The sequence of the symbols corresponds to the respective treatment.

The fact that at those soils dominate the clayey minerals with low specific surface and adsorption capacity have to be noted. Their electric-negative charges exert too slight induction effect on the next organic layers. The kinetic parameters obtained by electrodialysis of the organoclayey models on the basis of the kaolinite are with approximately equal values to the corresponding to the slightly connected calcium fraction (Table 4). Can been expected that at soils enriched with montmorillonite minerals the effect will be more different.

In this relation the investigation is extended by inclusion the organomineral samples of Vertisol (EV – Ca – OM – Ca) and kaolinite (Kt – Ca – OM – Ca) too (table 3; table 4). The comparative analysis of the obtained results shows that the saturation of montmorillonite with humic compounds in initial stage of humification (Mt – Ca – OM – Ca) decreases essentially the sorption capacity. This action is reduced mainly to block of the adsorption centers of the basal surfaces (Table 1, Table 3). This result is probably an effect of aggregation of the mineral fractions which hampers the access to their inter-packet areas.

Table 4. Kinetic parameters of montmorillonite (Mt), kaolinite (Kt) and studied soils (Distric Planosol-DPl and Vertisol – V) and of their associates with humus

Samples	Ca_1, $cmol.kg^{-1}$	K_1, min^{-1}	Ca_2, $cmol.kg^{-1}$	K_2, min^{-1}	ΣCa, $cmol.kg^{-1}$
Mt-Ca	26.6	$5.8.10^{-4}$	36.8	$2.1x10^{-4}$	63.4
Mt-Ca-OM-Ca, hum	47.2	$1.2x10^{-3}$	39.0	$1.7x10^{-4}$	86.2
V	16.1	$3.0x10^{-2}$	17.4	$1.5x10^{-4}$	33.5
V-Ca-OM-Ca, hum	21.3	$1.1x10^{-2}$	22.4	$2.0x10^{-4}$	43.7
Kt-Ca	3 hours desorption				
Kt-Ca-OM-Ca, hum	4 hours desorption				
DPl	1.6	$3.6x10^{-2}$	lack		1.6
DPl-Ca	4.0	$3.4x10^{-3}$	5.3	$1.0x10^{-3}$	9.3
DPl-Ca-OM-Ca,hum	14.6	$2.5x10^{-3}$	9.7	$5.2x10^{-4}$	24.3

OM – samples treated with humic compounds: Hum – during humification process.
The sequence of the symbols corresponds to the respective treatment.

At the samples obtained by Eutric Vertisol (EV – Ca – OM – Ca) the situation is not much different with this difference that the quota of the centers on the side areas is increased more then twice (Table 3).

The results of analysis of the obtained models on the bases of kaolinite (Kt – Ca – OM – Ca) are quite different (Table 3). The sorption capacity after saturation with humic compounds strongly increases mainly at the expense of the side areas. The experimental data for Eutric Planosol are unidirectional regarding the strongly increase of the sorption capacity. This increase is mainly at the expense of the basal surfaces.

The assumption for better structure-formed ability of humic substances in advanced stage of carbonization at vertisol and kaolinit is confirmed. The rate constant of calcium extraction from montmorillonite containing mainly newly formed humic substances (Mt – Ca – OM – Ca) is $1,2.10^{-3}$ while for the initial model Mt – Ca which contains at least a minimal quantity of humic substances in more advanced humification stage, $k_1=5,8.10^{-4}$. The same is observed at the two models on the Eutric Vertisol.

The case at the model with kaolinite, where the calcium extraction is done very rapidly, is similar. After saturation with Ca (EPI – Ca) or with Ca and humic substances (EPI – Ca – OM) the extraction is not finished completely after 8 hours' duration of the process at Eutric Planosol. Two fractions of Ca with faster increase of the quantity of the slighter connected are observed.

CONCLUSIONS

The presented results show a different influence of the humic substances on the sorption properties of clayey minerals from different type. It is determined that after processing with newly formed humic substances:

- The monttmorillonite materials change slightly their sorption ability towards Ca;
- The kaolinite minerals significantly increase their sorption capacity.

According to this, the soil adsorbent of the acid soils adsorbs considerably higher quantity of Ca after treatment with humic compounds. The change is insignificant at Eutric Vertisol.

It is determined that newly formed humic substances reduce essentially the sorption capacity of montmorillonite. This is mainly at the expense of the permanent charges on their basal surfaces. The reduction degree depends on the common influence of the humic substances and the corresponding cation type. The action of the monad cations (K, Na) is more strongly expressed compared to bivalent (Ca, Mg). Simultaneously is observed comparative increase of the quantity of permanent charges on the side surfaces of the montmorillonite as by influence degree on this parameter the following row is formed: Na>Mg>K>Ca.

The mobility of the cations depends on their localization in the structure of soil adsorbent:

- The cations, situated on the surface of its external organic layer and the cations constructed the bridge bunch between the external and the internal layer have similar but slight stability regarding their electrochemical extraction;
- The cations connecting the primary organomineral kernel with the internal organic layer of the adsorbent and the cations building aggregative bridge bunch between the separate colloid units are connected comparatively more closely and are extracted at lower speed by electrodialysis;
- The cations, included in the primary organomineral matrix are not extracted by electrochemical extraction.

Also important is the performed information about the connection between the evolution stage of humic substances and ion exchange ability of the soil adsorbent. It can be suppose that the input of the organic components in more advanced stage of humification will raise the connection solidity of Ca with the soil colloids. This discovers possibilities for raising the effectiveness of liming of the acid soils through their treatment with suitable organomineral lime mixture.

REFERENCES

Chassin, P., B. Le Berre, N. Nakaya, 1978. Hydratation des associations montmorillonite acides humiques, Clay Miner, 13, 1, 1-16. (Fr)

Chassin, P., N. Nakaya, B. Le Berre, 1977. Adsorption des acides humiques et fulviqes par la montmorillonite, Clay Miner, 12, 3, 261-271. (Fr)

Ganev, S., A. Arsova, 1980. Methods for determination of the strongly acidic and weakly acidic cation exchange in soils. Sofia, Soil Sci. and Agrochemistry,15 (3): 22-33 (Bg).

Greenland, D. J., 1971. Interactions between humic and fulvic acids and clays, Soil Sci., 11, 34-41.

Kononova, M. M., 1966. Soil organic matter. It's nature, it's role in soil Formation and Soil Fertility. 2nd English Ed., Pergamon Press Inc., Elmsformd M.V., 544 pp.

Koyama, M., 1995. Adsorption of humic acid on Ca-montmorillonite, Soil Sci. and Plant Nutr., 41, 2, 215-223.

Raychev, T., 1996. Influence of organo-mineral interactions on colloid-chemical state of the soil adsorbent. D. Sci. Thesis, "N. Poushkarov" Inst., Sofia, 161 pp. (Bg).

Schnitzer, M., 1969. Reactions between Fulvic Acid a Soil, Humic Compound and inorganic Soil Constituents, Soil Sci. Amer. Proc., 33, 75-81.

Schnitzer, M., 1991. Soil Organic matter – The next 75 years", Soil Sci., 151, 1, 41-59.

Schnitzer, M., H. Kodama, 1966. Montmorillonite: Effect of pH on its adsorption of a soil humoc compound, Science /Waschington, DC/, 153, 70-71.

Stevenson, F. J. S., 1982. Humus chemistry, John Wiley & Sons, Somerset New York, p.17.

Tarchitzky, J., Y. Chen, As. Banin, 1993. Humic Substances and pH Effects on Sodium and Calcium-Montmorillonite. Flocculation and Dispersion, Soil Sci. of Am. J., 57, 2, 367-372.

Tisdall, J. M., J. M. Oades, 1982. Organic matter and water stable aggregates in solis, J. Soil Sci., 33, 141-163.

INFLUENCE OF HUMUS SUBSTANCES ON HYDROPHILICITY AND ENERGY STATE OF SOIL ADSORBENT

Raytchev T.[1], Rousseva S.[1], Mehandjiev D.[2]
HajnosM.[3], Sokolowska Z.[3]

[1] *N. Poushkarov Institute of Soil Science, 7 Shosse Bankja Str., 1080 P.O. Box 1369, Sofia, Bulgaria*
[2] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Science, Sofia, Bulgaria*
[3] *Institute of Agrophysics, Polish Academy of Sciences, 4 Doswiadczalna Str., P.O. Box 201, 20-209 Lublin, Poland*

Abstract

The humus substances have been studied to establish their influence on the energetic parameters of the soil adsorbent at two soils of diverse genesis (Eutric Planosol and Eutric Vertisol), which enable two-way aggregation of the humus with the highly dispersive minerals – on account of the residual inter-molecular forces and cation bridges, as well as through valence bonds.

Established better hydrophilic properties of the soil adsorbent of the Eutric Vertisol compared to the Eutric Planosol give groundings to assume that it is due to (i) better balance of the colloid components included in the organo-mineral associations; (ii) domination of clay minerals of montmorillonitic type in its structure and (iii) higher degree of maturity of the organic components building its humus system.

Observed impact of the humus substances on the values of the energetic parameters of the soil adsorbent interpreted with the fact that their aggregative stability depends to a great extent on the pH, the ion force of the solution and the genetic features. Grounds for such an assumption are based on the understanding that the underlying structural unit of their lyophilic sols is not the mycelium but the highly hydrated macro-molecules. Availability of electric and hydrous cover on the surface of their particles determines their stability. The elasticity and the high activeness of the organic fragments facilitate the formation of adsorption-solvate layers on the surface of the mineral colloids. The energetic state of the mineral surfaces modified in this manner is defined by the hydration of the exchangeable ions as well as by the manner of their engaging in the structure of the soil adsorbent.

It is assumed that the lower elasticity of the polymer molecules included in the composition of soils of acid reaction is due to their well developed peripheral part ant the high number of acid functional groups. The spatial disturbance reduces the homogeneity in the orientation of the water molecules included in the hydrous cover and this is reflected on the values of the differential entropy. There is a better arrangement in the structure of the hydrous layer (lower values of the molar entropy) at the Eutric Vertisol. The integral and the molar heats of the two soils equalize in absence of humus but their values still remain higher for the Eutric Vertisol.

INTRODUCTION

The soil adsorbent manifests itself as a macro-anion with different centres of acid nature in conformity with the genesis of its formation. The origin, distribution and strength of these centres are a consequence of the nature of the colloid organization and the existing porous structure. Simultaneously, the strongly expressed electronegative character of the mineral kernel of the adsorbent causes induction effect also on the surface charges of the bounded with it adsorption layers of soil organic matter.

The activity of the adsorption centres determines the type of the reactions occurring in the system solid phase – soil solution. To a great extent, this requires knowledge on the energetic effects accompanying the adsorption processes on the surface of the soil adsorbent. The studies in this direction show that the amount of the permanent and the variational charges and the relations between them corresponds to the dominating type of clay minerals. This impact is expressed more strongly on the variational charges, which depend on the mineral type. Their densities decrease strongly when minerals of montmorillonitic type dominate, which is due to their much higher surface area compared to the minerals of kaolinic type.

It can be assumed that the type of the humus system and the manner of binding of the humus components with the soil clays determine to a certain extent the energetic inhomogeneity of the organo-mineral adsorbent.

This is a reason for studying the influence of the humus substances on the energetic parameters of the soil adsorbent of two soils of diverse genesis, which enable aggregation of the humus with highly dispersive minerals in two different ways – on account of the residual inter-molecular forces and cation bridges as well as through valence bonds.

MATERIALS AND METHODS

The study has been accomplished with soil samples from three horizons of two soils: Eutric Planosol (Velchevo village, Lovech district) – horizon A_1 (0 – 15 cm); horizon B_2 (62 – 82 cm); horizon C_1 (112 – 140 cm); Eutric Vertisol (Sretets village, Stara Zagora region) – horizon A_{pl} (0 – 25 cm); horizon B_1 (62 – 90 cm); horizon C_1 (120 - 130 cm).

The Eutric Planosol is developed on acid parent materials (sandstone). It has well expressed texture differentiation with respect to the profile distribution of the clay fraction the soil reaction changes from strongly acid (pH 5.0 in hor. A) to neutral (pH

6.8 in hor. B). The clay minerals in the top horizon (hor. A_1) are represented mostly by aluminiferous chloride (21%), hydro-mica (16%) and kaolinite (16%) (Atanassov, 1977; Atanassov and Dimitrov, 1976). The dominating clay mineral in the illuvial horizon (hor.B_2) is montmorillonite (37%), followed by hydro-mica (19%) and kaolinite (14%). There is similar distribution of clay minerals and the other mineral components in the horizon C_1, but the content of the montmorillonite is the highest (44%) there.

The humus system of this soil is of evident fulvic type of humus components. The polymeric molecules included in composition of the circulation fraction are of low elasticity, which is a consequence of well developed peripheral part they have and the high amount of acid functional groups. The acid reaction is a precondition for development of bonds between the organic and the mineral components of the soil adsorbent on account of the residual inter-molecular forces and cation bridges as well as through valence bonds. This is accomplished with the contribution of the positive variational charges on the lateral surfaces of the dominating clay minerals of kaolin type.

The Eutric Vertisol is characterized by clayey texture without pronounced differences in the clay and the fine silt fractions between the individual genetic horizons. Clay is the dominating texture fraction in this soil. There are no significant changes in the distribution of clay minerals along the soil profile. The montmorillonitic group is dominant (~ 70%), followed my illite (~ 14 %) and kaolinite (~ 10%). There are also certain amounts of hydrogoethite as well (~ 5.0%) (Atanassov, 1977). The value of pH varies from 7.3 to 8.0. Organic components with well developed kernel part dominate in the composition of the humus system while their acid groups are neutralized to a great extent by the available bases. Their presence and the slightly alkaline reaction exclude the opportunity for a direct valence binding with the clay minerals.

The study has been accomplished with initial soil samples and their clay fractions extracted by the method of Aydinyan (1966) as well as with samples treated with H_2O_2 (Jackson, 1956). The specific surface area (S_{BET}) of the initial and the treated samples has been determined by the BET method using data for low-temperature adsorption of nitrogen vapours (Brunauer et al., 1938; Gregg and Sing, 1967). The amount of the adsorptionally bounded water and the energetic parameters of the organo-mineral surfaces have been determined by the adsorption isotherms obtained through adsorption of water vapours up to a relative pressure P/Po = 0.94 at two temperatures ($T_1 = 20^oC$ and $T_2 = 30^oC$). The calculations have been accomplished by the following formulas (Kiselev, 1958; Komarov, 1977):

1. Differential heat of sorption $Q_\alpha = R\frac{T_1 \times T_2}{T_2 - T_1}\left(\ln\frac{P_2}{P_1}\right)$, where P_1 and P_2 are the equilibrium pressures of the adsorbate at temperatures above the adsorbate respectively T_1 and T_2 and the same amount of adsorbed matter (α). The values of P_1 and P_2 have been determined graphically.

2. Differential change of the free energy $-\Delta\mu = RT\ln\frac{P_o}{P}$;

3. Change of the differential molar entropy $\frac{\partial \Delta S}{\partial \alpha} = \frac{-(Q_\alpha - L) - \Delta\mu}{T}$, where L is the heat of condensation (Kiselev, 1958; Komarov, 1977).

RESULTS

Established differences in the character of the organic matter between the two soils give reason to assume diverse influence on their hydrophylity as well. The obtained results for the heat of wetting (Q) and for the molar heat of wetting ($Q/\alpha_{0.94}$) before and after treatment with hydrogen peroxide show a strong increase of their values in presence of humus. The availability of polar radicals on the surface of the solid phase is a precondition for establishment of a hydrogenous bond between them and the water molecules, which is reflected in the heat of wetting and it increases (Ovcharenko, 1960). The values of Q and $Q/\alpha_{0.94}$ before the removal of the organic matter are higher for the samples of the Eutric Planosol (EPl). This can be due to the better developed peripheral part of the polymer molecules and the availability of a larger number of functional groups capable of holding the water molecules through hydrogenous bonds. In this case, the increased values of these parameters are mostly on account of the hydrogenous binding since the influence of the coordination bond between the water and the exchangeable cations has been recognized to a slighter degree. This is proved by the decrease of Q and $Q/\alpha_{0.94}$ and their equalization after treatment with hydrogen peroxide. The molar heat of wetting varies in the limits 7.0 – 7.5 kJ/mol, an interval, close to that established by Ovcharenko (1960) during their studies on the hydrophylity of clays and clay fractions extracted from different soils. It can be expected that the removal of the organic matter would result in increased values of the heat of wetting for the clay fractions of the Eutric Vertisol (EV) as far as the content of exchangeable ions is significantly higher there. The observed reduction of this parameter in this case can be explained by the differences in the mineral composition between the two soils. A part of the liberated heat is lost for swelling of the minerals with mobile crystal lattice. The montmorillonite dominates in the clay minerals' content of the Eutric Vertisol. It is cleaner, with less disturbed structure and capable of swelling more strongly, which is related to a loss of energy and this is reflected in the total heat effect. From its side, the bound water related to unit weight and unit area varies slightly for both soils and it is not possible to obtain insufficiently reliable information on the hydrophylicity of the soil samples in general.

Comparisons of the data for the soil samples show that the adsorptionally bound water of EPl increases with the depth of the soil samples. This is related to the increase of the contents of clay fraction and minerals of montmorillonitic type down the soil profile. There are no such differences for the EV and the values of $\alpha_{0.94}$ are close, being always higher than these for the EPl. The change of the ratio $\alpha_{0.94}/S_{BET}$ follows the same tendency for the soil profile depths in both soils but the respective values are higher in the EPl (excluding the horizon A). This is reflected on the activity of the surface with respect to the sorption of water – there are more active centres per unit area of the EPl, which are capable of holding the water molecules.

The exchangeable ions play a role of active centres and regulators of the inter-layer adsorption of polar substances from the montmorillonite and the vermiculite Tarasevich and Ovcharenko (1975). The substitution of the natural exchange complex of these minerals with other inorganic cations results to significant changes in their adsorption properties – the exchangeable cations affect not only the water amount inside the crystal lattice but also the package density of the adsorbed water molecules. For that reason the specific surface area, determined from the adsorption of water vapours would change with the modifications of the exchangeable complex, despite the constant geometric surface area of the minerals. Therefore, the surface area determined by water vapour does not give a real representation of the extent of the hydrous area. This is proved also by the results obtained after calibration from nitrogen adsorption. Established values for the area of the water molecules (ω_{H2O}) in the adsorption layer differ significantly from the value used in the calculations of the surface area (ω_{H2O} = 10.8 Å^2). Extremely high values result from the recalculation of the surface area with the newly obtained areas, which do not correlate with the possible size of the area even for the pure clay minerals contained by the clay fraction (Tarasevich and Ovcharenko, 1975). That is why the adsorption measurements for nitrogen are used in the study.

The values of $\alpha_{0.94}$ for the clay fractions do not change significantly after treatment with hydrogen peroxide whereas it should be observed a reduction of the amount of adsorptionally bound water. This is likely to be related to release of new surfaces, already available for the water molecules – the specific surface area determined from nitrogen vapours increases for most of the samples after their treatment with hydrogen peroxide. The acid reaction generates conditions for valence binding between the humus substances and the lateral surfaces of the clay minerals of kaoline type for the samples isolated from the horizons A and B of EPl. The attack with hydrogen peroxide is not sufficiently aggressive for their disintegration. This is reflected on the absence or the slight change of the initial specific surface area after this treatment. There are no conditions for generating similar bond at the samples isolated fro the same horizons of the EV where the disaggregation is more complete and the released surface area is larger.

Decrease of the heat of wetting is established for all the samples from clay fractions when the moisture content increases and the curves $Q = f(\alpha)$ approach to the axis of the abscissa at relatively high moisture contents that is shown in Figs. 1-6.

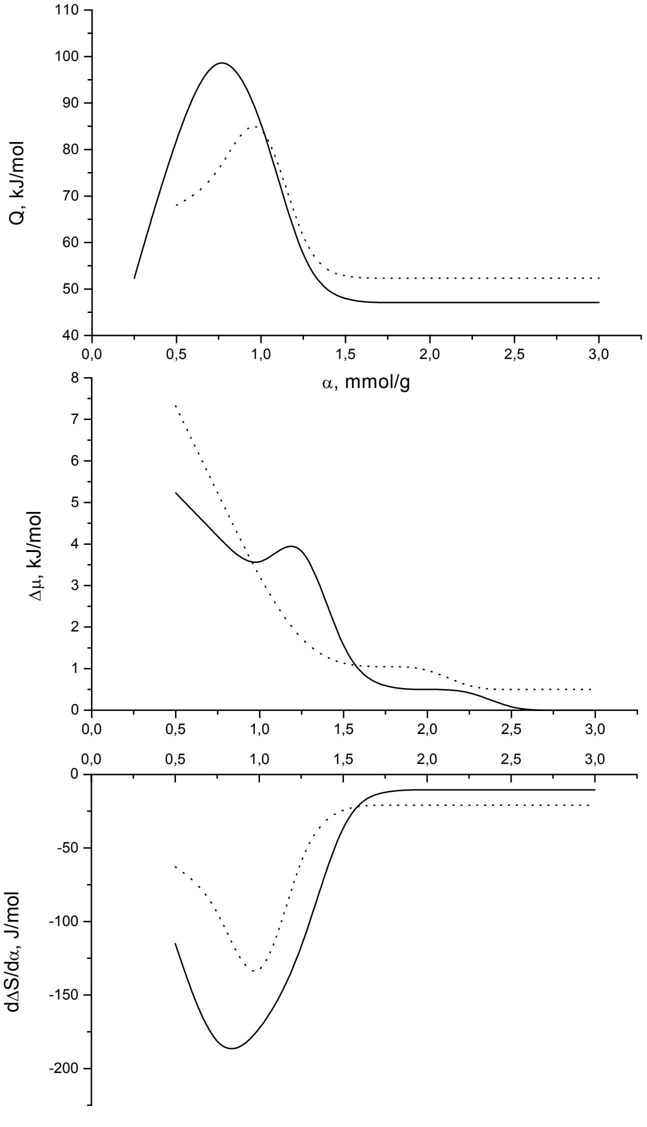


***Fig. 1.** Changes of the thermodynamic characteristics of clay fraction of A horizon from Eutric Planosol before (—) and after (···) treatment by H_2O_2*

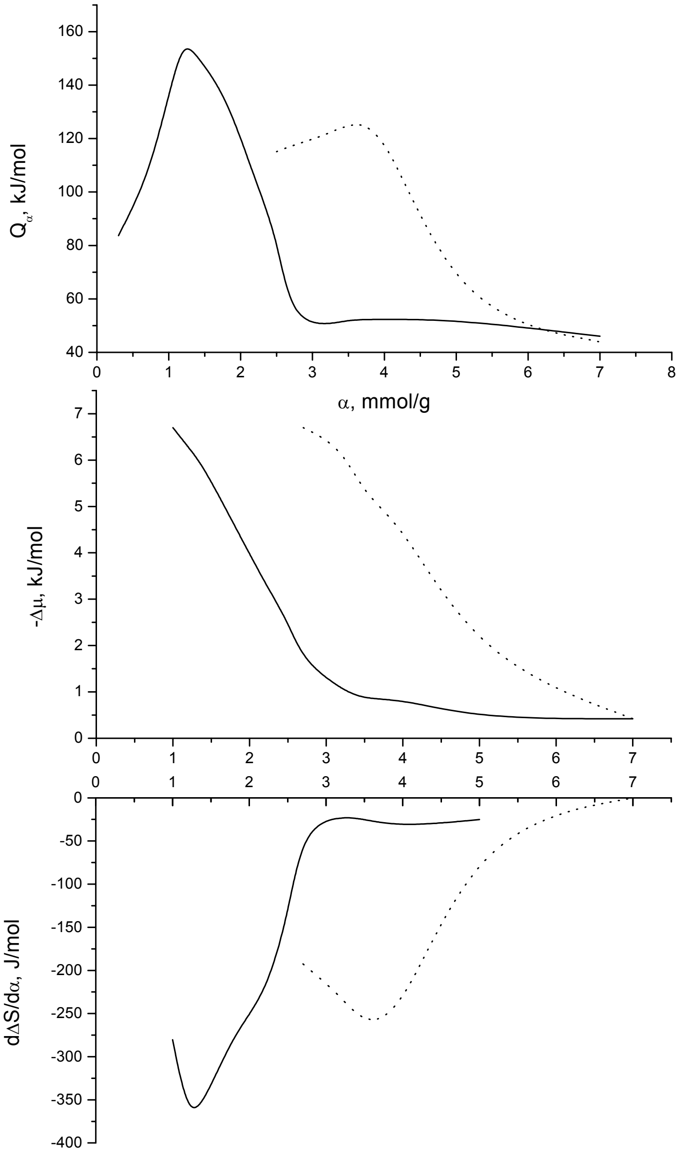


Fig. 2. *Changes of the thermodynamic characteristics of clay fraction of B horizon from Eutric Planosol before (—) and after (···) treatment by* H_2O_2

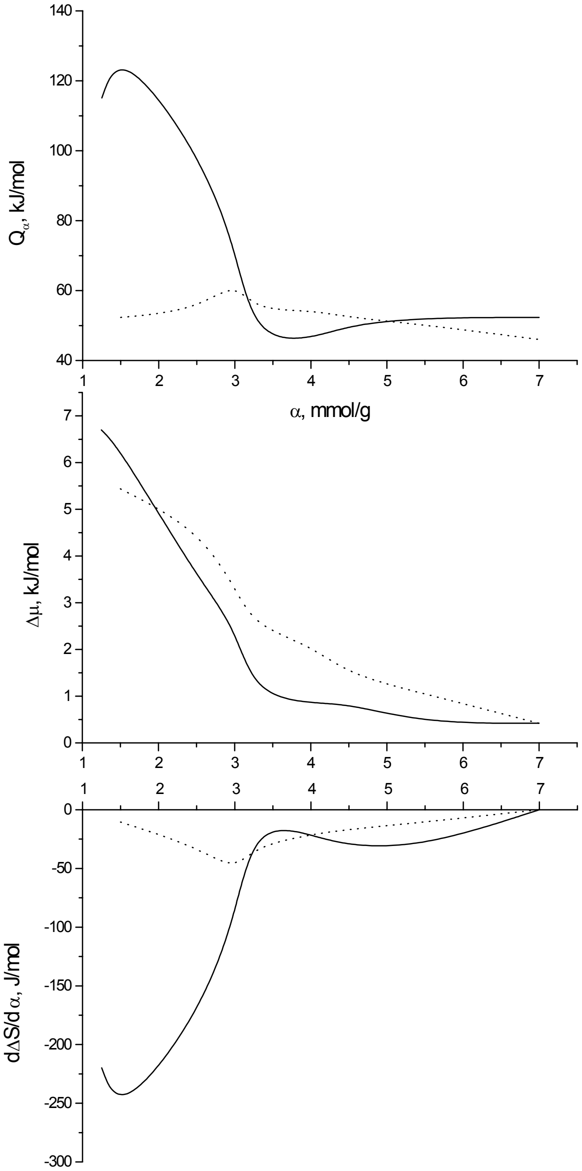


Fig. 3. *Changes of the thermodynamic characteristics of clay fraction of C horizon from Eutric Planosol before (—) and after (⋯) treatment by* H_2O_2

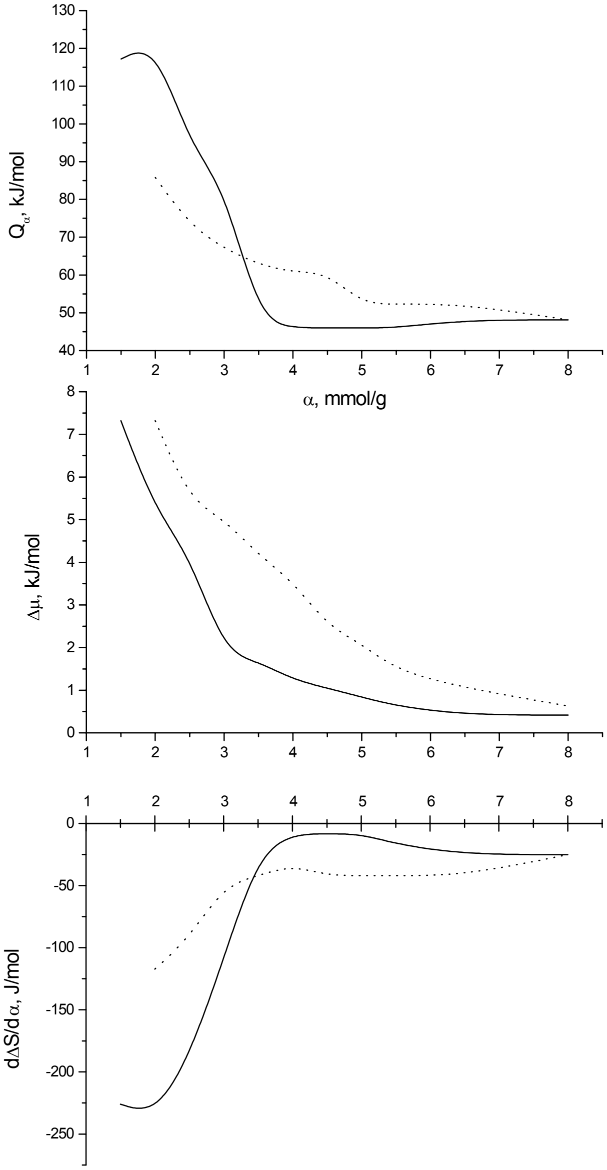


Fig. 4. *Changes of the thermodynamic characteristics of clay fraction of A horizon from Eutric Vertisol before (—) and after (···) treatment by* H_2O_2

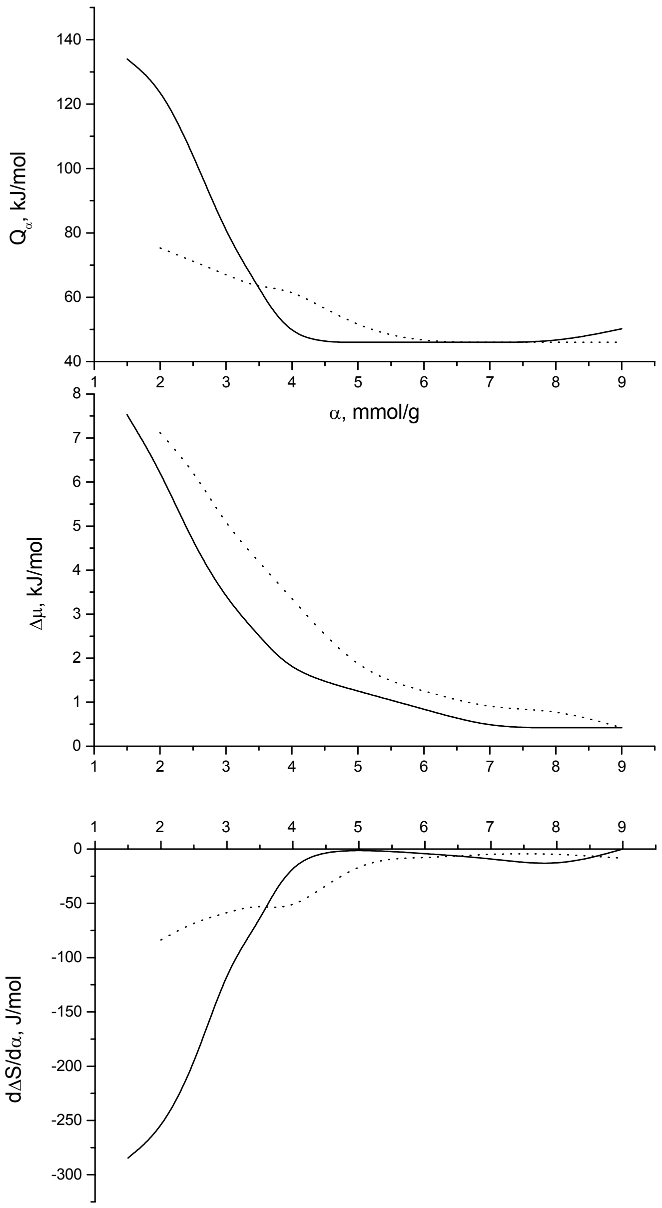


Fig. 5. *Changes of the thermodynamic characteristics of clay fraction of B horizon from Eutric Vertisol before (—) and after (···) treatment by* H_2O_2

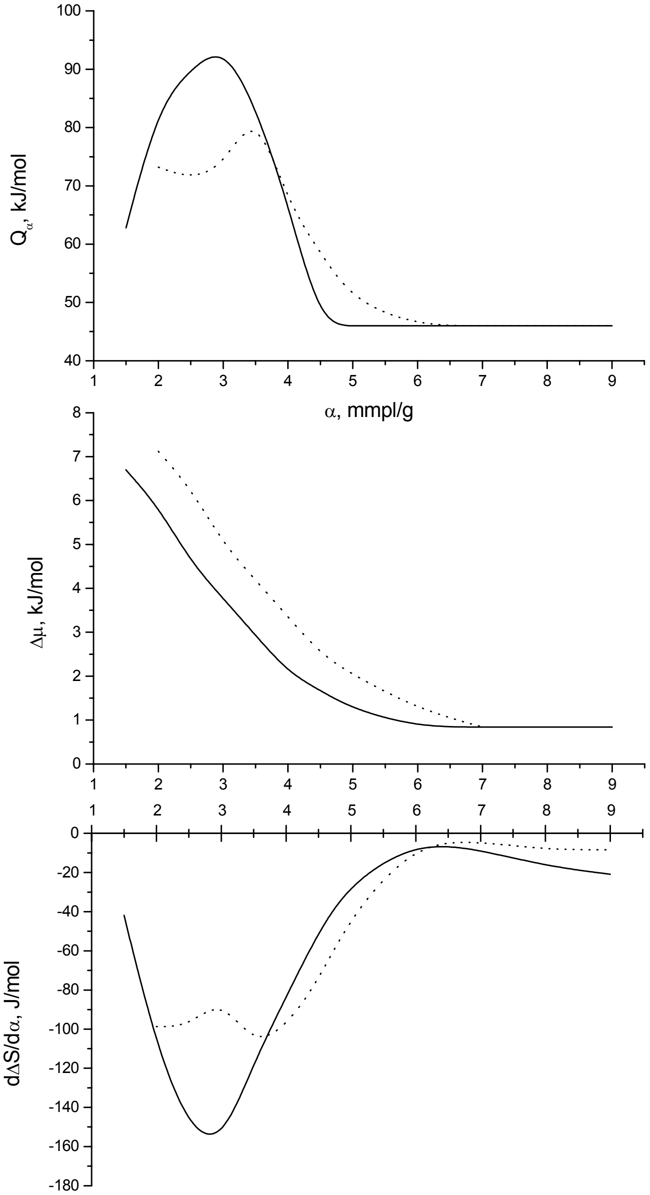


Fig. 6. *Changes of the thermodynamic characteristics of clay fraction of C horizon from Eutric Vertisol before (—) and after (···) treatment by* H_2O_2

The differential heat of wetting initiates reduction at $\alpha = 1$ mmol/g for the samples from EPl before the removal of the organic matter. After the organic matter removal, the decrease of Q_α starts at higher values of α ($\alpha = 3$ mmol/g) – excluding horizon A. Compared to the EPl, the values of Q_α for the samples from EV start reduction at higher values of a ($\alpha > 2$ mmol/g). There is also displacement towards higher values of α after the removal of the organic matter at EV but it is less revealed compared to the EPl.

The mode of the curves $\frac{\partial \Delta S}{\partial \alpha} = f(\alpha)$ is similar to that for $Q = f(\alpha)$. The presence of minimum is related to the abrupt decrease in the mobility of the sorbate molecules at their interaction with the primary active centres. The entropy increases during the transition towards sorption on the secondary centres, but remaining still negative which shows that the degree of arrangement of the water molecules decreases. The increase of the entropy after the removal of the organic matter for both soils is related with the lower degree of orientation of the adsorbed water molecules on the modified surface. The differences in the mode of the curves after the removal of organic matter for the samples from EPl are a reflection of the stronger influence of the humus in this soil.

The analysis of the curves of the free energy ($-\Delta\mu = f(\alpha)$) shows that it decreases with the increase of the content of sorbed water, while the values of maximal effective work for the samples from the same soil are similar. The smooth decrease of the considered curves is an indication for: (a) absence of chemisorption and (b) dissimilar reaction of the components in the system with regard to the applied impact. This impedes the filling in the successive layers of the inter-package space of the minerals with mobile crystal lattice (Tarasevich and Ovcharenko, 1975). The latest is caused by the fact that the study has not been accomplished with individual minerals of well defined crystal structure. Instead, it is their natural mixture, which components react dissimilarly and unsimultaneously with regard to the adsorption.

When discussing the results obtained in this study, the following circumstances should be considered: the total sorption heat is composed from a proper heat of sorption determined by the interaction between the water and the active centres of the sorbent and the heat of interaction between the sorbed molecules; the sorption heat of the secondary and the next sorption centres is lower than the sorption heat of the primary; it should be considered the influence of the hydrogen binding, on which account the total energy of interaction sorbate-sorbent increases; the sorption heat of the substances, forming hydrogen bond is always higher than the sorption heat of substances with similar structure, but not forming similar bonds.

Some physicochemical characteristics of the studied soils along with numerical data derived in this paper are summarized in Tab. 1.

Table 1. Termodynamic characteristics of soils and clay fractions (particles < 2 μm), extracted from Eutric Planosol (EP) and Eutric Vertisol (EV)
Soil – initial soil sample; 1 – initial clay sample; 2 – clay after treatment with H_2O_2; S_{BET} – specific surface area (Brunauer et al., 1938); $\alpha_{0.94}$ – adsorptionally bound water per unit mass маса (mmol/g); $(\alpha_{0.94})/ S_{BET}$ – adsorptionally bound water per unit area, (mmol/m^2); Q – total heat of wetting, J/g; Q/ $\alpha_{0.94}$ – molar heat of wetting, kJ/mol

Soil/ Horizon		Sample	S_{BET}, m^2/g	$\alpha_{0.94}$ mmol/g	$(\alpha_{0.94})/ S_{BET}$ mmol/m^2 x10^2	Q, J/g	Q/ $\alpha_{0.94}$ kJ/mol	C, %
EP	A_1	Soil	21.2	1.2	5.7			1.38
		1	31.3	2.6	8.3	39.3	15.1	1.88
		2	36.6	5.2	14.2	36.8	7.1	0.74
	B_2	Soil	54.4	5.5	10.1			0.93
		1	85.3	10.1	11.8	158.6	15.7	1.34
		2	86.3	9.3	10.9	73.2	7.9	0.59
	C_1	Soil	48.3	5.2	10.8			0.32
		1	81.4	8.8	10.8	146.5	16.6	0.56
		2	82.4	9.0	11.0	67.8	7.5	0.37
EV	A_{pl}	Soil	82.3	6.6	8.0			1.95
		1	90.0	11.2	12.4	130.0	11.6	2.24
		2	118.4	10.8	9.1	75.3	7.0	0.68
	B_1	Soil	76.6	6.4	8.4			1.22
		1	94.5	10.3	10.9	106.7	10.4	1.75
		2	111.4	10.8	9.7	75.3	7.0	0.53
	C	Soil	78.8	5.8	7.4			0.70
		1	131.0	10.1	7.7	119.3	11.8	1.81
		2	124.9	12.0	9.6	91.7	7.6	0.44

Based on the obtained results, the sorption of water on the clay fractions of the studied soils can be presented as follows: The first portions of water are absorbed most intensively accompanied by release of significant amount of heat. It is always higher in a presence of humus. The high negative values of the differential entropy at not large fills show that: (a) the absorbed H2O molecules are firmly bound with the sorption centres and (b) they form relatively well-arranged structures on the organo-mineral surfaces. Besides, the available organic matter influences the degree of arrangement of the sorbed water molecules at the initial process of sorption and this influence is stronger at the EPl. The adsorption of the following portions of water occurs less intensively compared to the first stage – the interaction between the already sorbed molecules and these which sorption is in a progress is considerably decreased.

CONCLUSIONS

The established better hydrophilic properties of the soil adsorbent of Eutric Vertisol compared to these of Eutric Planosol give reason to assume that it is a reflection of: (a) better balance of the colloid components included in the organo-mineral association, (в) the domination of clay minerals of montmorillonitic type in its structure and (c) the higher degree of maturity of the organic components constructing the humus system of this soil.

The observed impact of the humus substances on the values of the energetic parameters of the soil adsorbent can be explained by the fact that their aggregative stability depends to a large extent on the pH, the ion force of the solution and the genetic features. The basic structural unit of the lyophilic sols is not the mycelium but their strongly hydrated macro-molecules. The availability of electric and hydrous coat on the surface of their particles determines their stability. The elasticity and the high activation of the organic fragments facilitate development of adsorption-solvate layers on the surface of the mineral colloids. The energetic state of the so modified mineral surfaces is conditioned by the hydration of the exchangeable ions as well as by the manner of their inclusion in the structure of the soil adsorbent.

The lower elasticity of the polymer molecules included in the composition of soils of acid reaction is due to their well developed peripheral part ant the high number of acid functional groups. The spatial disturbance reduces the homogeneity in the orientation of the water molecules included in the hydrous cover and this is reflected on the values of the differential entropy. There is a better arrangement in the structure of the hydrous layer (lower values of the molar entropy) at the Eutric Vertisol. The integral and the molar heats of the two soils equalize in absence of humus but their values still remain higher for the Eutric Vertisol.

LITERATURE

Atanassov, Iv., 1977. Weathering and evolution of mineral part of the soils in Bulgaria. D. Sci. Thesis, Higher Agric. Inst., Sofia, p.566. (Bg)

Atanassov, Iv., D. N. Dimitrov, 1976. Distribution of the fine-dispersive minerals within the profile of light-grey gleyic soils. Soil Science and Agrochemistry, (XI) 3:17-25. (Bg)

Aydinyan, R. H., 1966. Accelerated method for extraction of soil clay and colloids using super-centrifuge. Agrochemistry, 6:151-156. (Ru)

Brunauer, S., P. H. Emmet, E. Teller, 1938. Adsorption of gases in multimolecular layers. Journal of American Chemical Society, 60, 309 – 314.

Gregg, S. J., K. S. W. Sing, 1967. Adsorption, Surface Area and Porosity. Academic Press, London and New York, p.304.

Jackson, M. L., 1956. Soil Chemical analysis – Advance course: Published by the author, Univ. of Wisconsin, Madison, Wis

Kiselev, A. V., 1958. The Structure and Properties of Porous Materials. Ed. D. H. Everett, F. Stone, London, p 195.

Komarov, V. S, 1977. Adsorbents and their properties, Publ. “Nauka I tehnika”Minsk. 248 p. (Ru)

Ovcharenko, F. D., 1960. Hydrophylity of Clays and Clay Minerals. Publ. AS USSR, Kiev: p. 292. (Ru)

Tarasevich, Yu. I., F. D. Ovcharenko, 1975. Adsorption of Clay Minerals. Publ. “Naukova dumka”, Kiev: p.352. (Ru)

Main symbols and abbreviations:

d – radius of slit-shaped pores calculated by desorption curve, Å
P/Po – relative vapour pressure
r – radius of bottle-shaped pores calculated by adsorption curve, Å
S_{BET} – specific surface area, $m^2\ g^{-1}$
S_p - surface area of the mesopores, m^2/g (mesopores – 2 ÷ 200 nm in radius)
V_m – monolayer capacity, $cm^3\ g^{-1}$
V_o – total pore volume, $cm^3\ g^{-1}$
V_p – volume of mesopores, $cm^3\ g^{-1}$
V_μ – volume of micropores, $cm^3\ g^{-1}$
ΔV – change the volume of the filled pores corresponding to Δr
HS_{back} - humus substance from back layer of SA
$HS_{int.}$ – humus substance from interaction layer of SA
$PM_{HS\text{-}clay}$ – primary organo-mineral matrix of Soil Adsorbent (SA)
$T_{8.2}$ - sum of negative charge on the surface exchangeable cations at pH 8.2, $cmol.kg^{-1}$
T_{SA} - the amount of the permanent negative charge, $cmol.kg^{-1}$
T_A - the amount of the variable negative charge, $cmol.kg^{-1}$
$\sigma_0 = (T_{8.2}/S_{BET})$, $cmol.m^{-2}$ - charge density
$\sigma_p = (T_{SA}/S_{BET})$, $cmol.m^{-2}$ - the permanent charge density
$\sigma_v = (T_A/S_{BET})$, $cmol.m^{-2}$ - the variable charge density

AUTHORS

Donov Danail	N. Poushkarov Institute of Soil Science, Sofia, Bulgaria ndonov@iss-poushkarov.org
Filcheva Ekaterina	N. Poushkarov Institute of Soil Science, Sofia, Bulgaria e_filcheva@abv.bg
Hajnos Mieczysław	Institute of Agrophysics PAS, Lublin, Poland mhajnos@demeter.ipan.lublin.pl
Hubenov G	N. Poushkarov Institute of Soil Science, Sofia, Bulgaria
Jokova Mariyka	N. Poushkarov Institute of Soil Science, Sofia, Bulgaria M_Jokova@abv.bg
Józefaciuk Grzegorz	Institute of Agrophysics PAS, Lublin, Poland jozefaci@demeter.ipan.lublin.pl
Mehandjiev D.	Institute of General and Inorganic Chemistry, Bulgarian Academy of Science, Sofia, Bulgaria
Paskaleva K	N. Poushkarov Institute of Soil Science, Sofia, Bulgaria
Raytchev Toshko	N. Poushkarov Institute of Soil Science, Sofia, Bulgaria dr_raytchev@abv.bg
Rousseva Svetla	N. Poushkarov Institute of Soil Science, Sofia, Bulgaria svetrou@yahoo.com
Sokołowska Zofia	Institute of Agrophysics PAS, Lublin, Poland sokolows@demeter.ipan.lublin.pl
Toncheva R	N. Poushkarov Institute of Soil Science, Sofia, Bulgaria