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INFLUENCE OF HUMIC ACID ON THE STRUCTURAL PROPERTIES OF KAOLIN - MERCURY POROSIMETRY STUDIES

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Abstract. The influence of the coverage of the kaolin surface with humic acid on its structural properties has been investigated. Humic acid (HA) was extracted with water from Ah horizon of an acid forest soil. The particle size of kaolin <2 μm were separated by suspension centrifugation, and kaolin consisted of 70% kaolinite. All samples were in powdered forms and, in addition, some selected samples were used as pellets. Textural analyses were performed by Carlo Erba Mercury Porosimeter Series 2000. The cumulative pore size distribution and the pore size distribution (PSD) curves for kaolin and kaolin with HA were analysed. Bulk density, surface area, average pore radius and the total porosity were calculated using cylindrical pore model. The study confirmed that humic acids play an imprtant role in the structure formation of kaolin. In powdered samples, the cumulative pore size distributions curves split into three groups having different pore volumes. This proved the existence of a dependence of pore volume on the added amount of humic acid. The lack of proportionality between the total pore volume and the humic acid concentration observed in this study may also indicate inhibiting influence of intermediate humic acid doses on flocculation. In kaolin which was initially wetted with distilled water, a fast decrease of total pore volume was observed. This may be explained by existence of mineral flocculation in distilled water.

Keywords: clay mineral, kaolin, humic acid, mercury porosimetry technique, structure

INTRODUCTION

The pore structure of clay minerals plays an important role in catalysis, soil science, engineering and other disciplines. Soils with more than 30-35% of clay tend exhibit the properties of the clay itself. Clay fractions of many types of soils contain appreciable quantities of montmorillonite, smectite, kaolinite and illite which strongly effect overall properties of soils.

The adsorption of organic compounds by clay minerals is directly related to numerous chemical and physical properties of the minerals and soil matrix. The complex formation between clays and humic substances has been approached from essentially two directions [37]. The first one ivolves the isolation and separation from soil of such complexes based on size and density, followed by their characterisation. Alternatively, the complex formation may be studied by allowing humic substances or their fractions to react with known clay minerals and examining the resulting complexes. The possible mechanisms of interaction between humic substances and clays have been discussed in reviews by Greenland [7] and Orlov [24].

The adsorption of humic and fulvic acids on montmorillonite, kaolinite and mordenite is closely related to the adsorption on Si and Al oxides [26]. The bounds of humic substances with 1:1 type layer silicates, kaolinite and halloysite, have been examined by several workes [3,5,8,12,16,24,26,27,35]. The influence of humic substance on flocculation of

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kaolinitic soil clays [20], water adsorption characteristics and fractal dimension of kaolin [33,34], and wettability of its surface [15] have been also investigated.

Mercury intrusion porosimetry has been applied by several workers in soil studies [2,4, 9,10,17-19,21,23,28,29-31,39]. This method is regarded as the most convenient, rapid and indispensable for obtaining a complete characteristic of the soil structure [21].

In this work the influence of humic acid on the porous system of powdered and compacted kaolin is studied.

MATERIALS AND METHODS

Humic acid (HA) was extracted with water from Ah horizon of an acid forest soil. The extracts were filtered by G4 glass bed, coagulated with HCl, washed with destilled water by centrifuging (until chloride ions were absent) and peptized in water. The final concentration of humic acid was $C_0 = 8$ g/dm^3.

The sample of kaolin was from Valencia, Spain. The specific surface area (determined from the BET equation by using water adsorption meaurements) of this clay mineral was 22.5 m^2/g, whereas its cation exchange capacity was 2.9 cmol/kg (Mehlich method). The particle size of clay <2 μm was separated by suspension centrifugation. This fraction of kaolin consisted of 70% kaolinite, 18% mica and of 12% quartz [39].

The susspension of the humic acid was diluted with destilled water to different concentrations ranging from $C = C_0$ to $C = 1/512\ C_0$ with C_0 being the initial concentration of the HA, what corresponds to the weight percent concentrations in the interval from 1.8 to 1.6 10^{-3}. The suspensions have been added to kaolin samples (ratio kaolin to suspension HA was 1:1), dried in room temperature and mildly grounded in a mortar. Samples were intensively mixed at the end of drying process. The sample with HA concentration of $C= 2C_0$ was made by adding a double amount of initial suspension of HA to kaolin sample.

Carlo Erba Mercury Porosimeter Series 2000 was used to determine the pore size and pore volume distributions in the range from 3.7 to 7500 nm radius by mercury intrusion. The samples were dried by owen-drying at 105°C and then outgassed before mercury intrusion.

All samples were in powdered forms and, in addition, some selected samples were used as pellets. The pellets were prepared at the pressure equal to about $5 \cdot 10^8$ Pa by the method describrd by Jańczuk and Białopiotrowicz [13]. Cumulative pore size distributions and the pore size distributions (PSD) for kaolin and kaolin with HA samples were analysed. Using the computer program Milestone 100 and cylindrical pore model the bulk density, surface area, average pore radius and the total porosity were calculated.

RESULTS AND DISCUSSION

Figures 1 and 2 display the cumulative pore volume curves of kaolin with humic acid in powdered and compacted (pellet) samples, respectively. The curves show the sum of mercury volume intruded into the pores versus their size. The shape of the curves changes with the amount of humic acid added to kaolin. In powdered samples, all cumulative curves split into three groups with different pore volume. These groups indicate the existence of a dependence of the pore volume on the added amount of the humic acid. Samples with an intermediate amount of humic acid (group 1 from 0.05 to 0.4 weight percent of humic acid) have the largest pore volume. Kaolin pre-wetted with distilled water and the samples with a small amount of HA (group 3 from $25 \cdot 10^{-3}$ to $6.5 \cdot 10^{-3}$ weight percent of humic acid) have the lowest pore volume. Indeed, cumulative curves for kaolin rich in humic acid (group 2 from 0.8 to 1.6 weight percent of humic acid) lie between the curves for samples with intermediate and low amount of humic acid. The highest cumulative pore volume was found in a sample of kaolin which has not been initially treated with water.

Flocculation and aggregation are the most important factors responsible for the structure formation. Thus, rapid decrease of the total

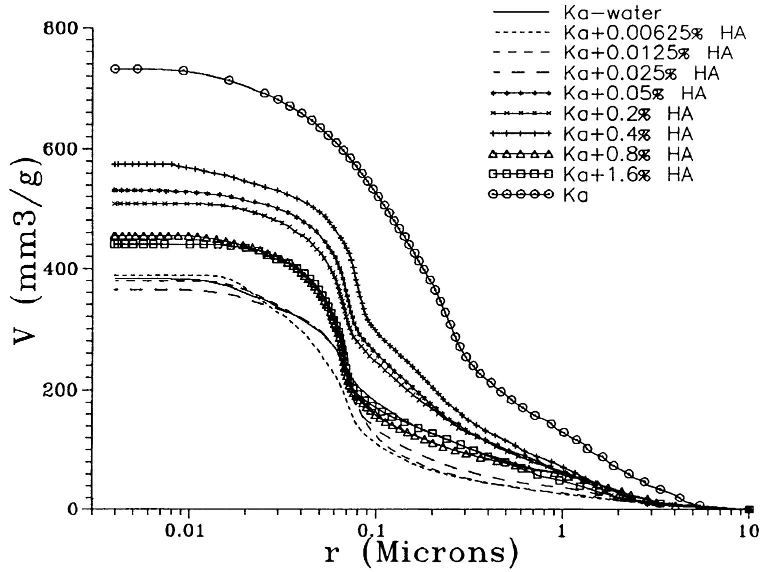


Fig. 1. Cumulative curves for kaolin and for samples of kaolin-humic acid in powder form.

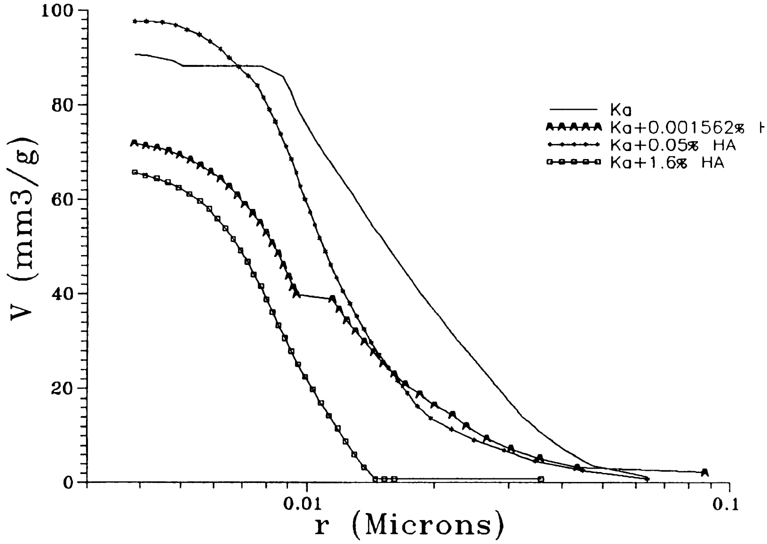


Fig. 2. Cumulative curves for kaolin and for samples of kaolin-humic acid in compact form.

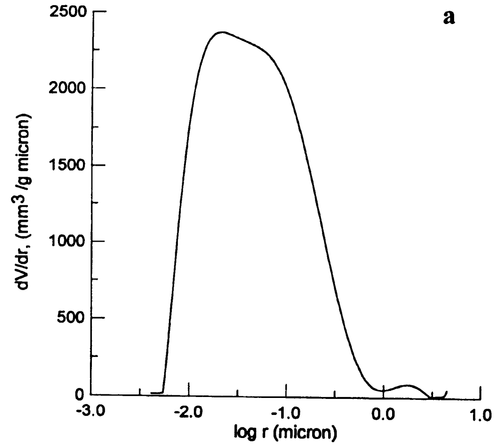
pore volume (from 780 to 380 mm^3/g) kaolin which was initially wetted with distilled water may be explained by the existence of mineral flocculation even in distilled water. Our observation are in agreement with the results of Arora and Coleman [1] and Kretzschmar [20] for kaolinites and soil clays containing kaolinit as a major clay mineral.

The observed dependence of the total pore volume on the amount of HA can be explained by considering processes of the kaolin structure formation and the influence of organic matter on these processes. As one can see from Fig. 1, low concentation of humic acid ($1.6 \cdot 10^{-3}$- $25 \cdot 10^{-3}$ weight percent) causes significant decrease in the total pore volume on average about 400 mm^3/g. This can probably be explained by the adsorption of HA on kaolin particles and by strong flocculation of this mineral. Further increase of the HA dose from 0.05 to 0.4 weigth percent leads an increase of the total pore volume in the samples to about 500 -570 mm^3/g . Most probably, this increase is the result of subsequent HA adsorption on kaolin, formation of steric, bigger floccules or aggregates and the creation of new pores. The highest HA concentration, 0.8 - 1.6 weight percent in our case, leads again to a decrease of the total pore volume to about 450 mm^3/g. This may be caused by organic molecules entering inside or floccules and aggregates and filling the pores which have been already formed. The lack of proportionality between the total pore volume and the HA concentration observed in this study may also indicate an inhibiting influence of the intermediate HA doses on flocculation. Similar conclusions have been drawn by Miller *et al.* [22] in their work on clays isolated from weathered soils in which kaoilnite was the major clay mineral.

Our considerations are also in agreement with common opinions on the role of organic matter in soil structure formation. It is known that the humic acid plays a major role in controlling the flocculation behaviour of kaolinitic soil fine clays [20]. Humic substances are organic polymers of high molecular weight and they are adsorbed on surface of kaolinite [26]. It is thus likely that a combination of electrostatic stabilization and steric stabilization leads to the effect of humic substances on the flocculation behaviour of clays, steric stabilization possibly being more important factor [20]. Jekel [14] demonstrated that three different humic extracts derived from surface water and groundwater decreased the collision efficiency in silica and kaolinite suspensions and adsorbed neutral molecules of high molecular weight were the most effective in stabilizing these suspension. In the pseudo-layered silicates, where entry of the organic matter into pore structure of the minerals is less restricted, the extent of adsorption is comparable to that for montmorillonite [37].

The packets of clay minerals have the charge on the in inner surface and on the edges. Total charge of a mineral particle is the resultant of the charge of the surface layer and the edges of the packet [36,38]. The existence of the negative surface charge and varying positive charge at the edges of the clay particles makes possible different ways of particle association. In general, there are three principal types of the associate ions: surface-surface; edge-edge and surface-edge. They may form various permanent structures [28,36,40]. In the case of kaolin suspensions, the type surface-edge association prevails. Thus association leads to the formation of steric floccules with a honeycomb like structure [40]. The sorption of humic acid depends on the sign of the mineral surface charge. Positively charged surfaces adsorb the humic acid to a greater extend than negatively charged ones [35]. An exposed surface of 1:1 kaolinite contains 50% Si and 50% Al sites as estimated from the chemical formula of kaolinite. Consequently, the adsorption envelope of organic matter by kaolinite is expected to resemble a combination of the adsorption envelopes observed for the Si and Al - oxide minerals. Since Si -oxide do not adsorb organic matter, the dominant adsorption sites on kaolinite appear to be the Al ones [26]. The analysis of the cumulative pore distribution curves does not allow us to draw any unequivocal conclusion concerning the structure of the kaolin modified with HA. However, one can postulate the hypothesis that the HA enters, fills and blocks the interlayer space of the mineral particles. A similar hypothesis has been developed in studies of changes in the surface area (BET equation, water vapour adsorption), contact angle and fractal dimension of samples of kaolin modified with HA [15,33,34]. Our data confirm that humic acids play an important role in the structure formation of kaolin.

Figures 3 and 4 show the pore size distribution curves (PSD) for kaolin and selected kaolin-HA samples in powdered and compacted



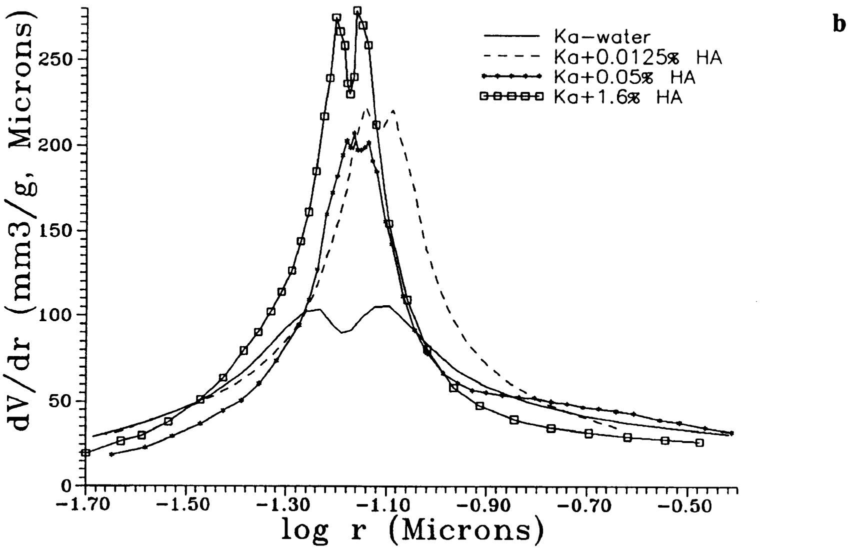


Fig. 3. Pore size distribution function (PSD) for dry kaolin (a) and sample of kaolin-humic acid (b) in powder form.

(pellet) forms, respectively. The PSD functions are similar for powdered samples (Fig. 3). They have similar shapes with a single peak which at its top divides into two maxima and with well-distinguished tail from the side of large pores. The pore size distribution for kaolin which was pre-wetted is broader and has maxima lower than other curves. The highest peak was found for the samples having the large content of humic acid and for sample of dry kaolin. The pore size distribution curves for kaolin with humic acid are shifted towards smaller pores radii as compared with kaolin (Fig. 3). The pore size ranges from 6 to 9000 nm in kaolin samples containing from 0.05 to 0.4 weight percent of HA was found. The maximum of the PSD curve is in the range of pore size radii of 50-60 nm, and the tail of the PSD represents pores of radii ranging from 400 to 9000 nm. For the group 2, i.e., for kaolin with maximum HA content, the pore radii are equal to 8-10000 nm; the maximum of the PSD is at 50-60 nm, and the tail is for the pore sizes of 150 to 10000 nm. In pre-wetted of kaolin, as well as in samples of group 3 poor in HA, pore sizes range from 6 to 9000 nm was observed. The PSD for the mineral with HA exhibits its maximum at pore radii range from 60 to 70 nm, and its tail covers pores from the range 200-9000 nm. There were two maxima on the PSD curve for kaolin wet with water. The first maximum at the radius of 65 nm was well expresed, smaller one, replacing the tail at the radius of 2000 nm. In dry kaolin, the total range of pore radii and the range of the tail of the PSD are the same as in the case of the samples from the group 1. The most significant difference is in the location of the maximum of the PSD, which is now at 200 nm. Generally, addition of HA causes narrowing the PSD curves, what indicates that from geometrical point of view these samples become more homogeneous.

For the compacted samples the pore volume is significantly lower (about 6 times) and close to about 90-100 mm^3/g (Table 1, Figs 2 and 4). All cumulative curves are between the curve for kaolin and for the sample with the maximum contents of HA. These results are dissimilar to the results obtained for powdered samples. Probably the effect of humic acid on

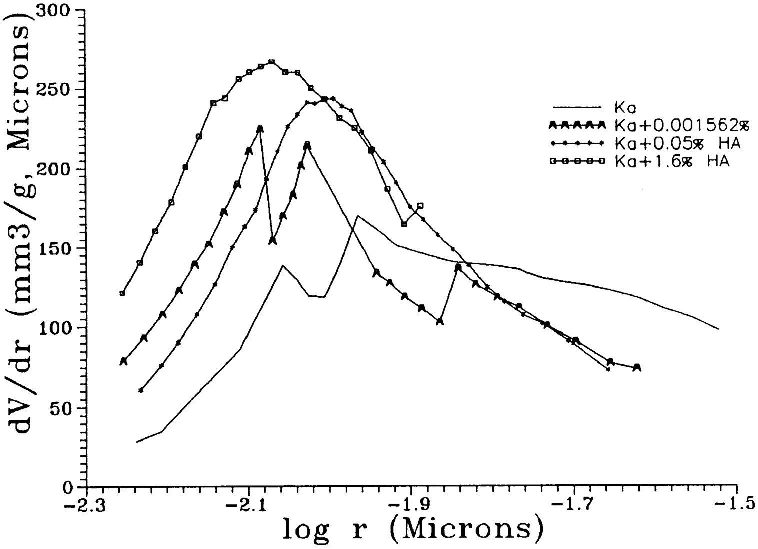


Fig. 4. Pore size distribution function (PSD) for kaolin and for sample of kaolin-humic acid in compact form.

Table 1. Structural parameters from mercury porosimetry data obtained with used of the cylindrical pore model

Sample	Total cumulative volume (mm^3/g)	Specific surface area (m^2/g)	Bulk density (g/cm^3)	Average pore radius (μm)	Total porosity (%)
			Powder		
Ka	730.59	15.74	0.80	0.199	58.81
Ka water	383.76	12.23	1.15	0.063	44.02
Ka+1/512 C$_o$	399.09	14.21	1.05	0.063	48.07
Ka+1/256 C$_o$	389.57	14.99	1.04	0.063	47.43
Ka+1/128 C$_o$	382.59	13.48	1.02	0.063	46.56
Ka+1/64 C$_o$	378.83	12.26	1.20	0.063	45.61
Ka+1/32 C$_o$	364.50	12.12	1.21	0.063	44.00
Ka+1/16 C$_o$	530.68	13.91	0.99	0.063	52.30
Ka+1/8 C$_o$	497.85	14.66	1.06	0.063	52.77
Ka+1/4 C$_o$	508.50	13.05	0.94	0.063	53.83
Ka+1/2 C$_o$	573.81	14.60	0.96	0.063	55.22
Ka+1 C$_o$	455.36	13.33	1.04	0.063	47.55
Ka+2 C$_o$	440.98	12.18	1.05	0.063	46.44
			Compact		
Ka water	86.74	11.49	2.07	0.0125	17.93
Ka+1/512 C$_o$	68.95	13.16	2.07	0.0079	14.30
Ka+1/16 C$_o$	63.97	15.70	2.12	0.0078	15.53
Ka+2 C$_o$	62.69	15.64	2.12	0.0079	13.27

mechanical properties of kaolin decreases with an increase of the amount of humic acid in mineral. A decrease of distances between mineral packets takes place during compaction remaining space is occupied by the molecules of HA. The adsorption of organic molecules on mineral surface and a decrease of distances between minerals particles are probably their flocculation occurs. Consequently, number of pores and their size decreases. It has been found that compaction causes an increase of orientational ordering of clay mineral particles, leading to the reduction of the free space between associates and, consequently, to changes in mineral structure [4,11,32,39]. Generally, we have founded pores from 3 nm to 50-60 nm in compacted samples, except for the sample containing the highest amount of HA where the range of pore radii was from 3 to 15 nm. These pores correspond to mesopore range, according to the IUPAC classification [5]. The PSD curves point also at the uniform structure of the compacted samples. Maxima on PSD curves correspond to pore radii of 15 nm for kaolin and at of about 9-10 nm for kaolin containg humic acid. The comparison of the dominating pore sizes with the average pore radii, with the total pore volume and with the total porosity (see Tabele 1) comfirms at the uniform structure of the compacted samples.

CONCLUSIONS

The influence of the coverage of the kaolin surface with humic acid on its structural properties was investigated. The study performed confirms that humic acids play an important role in the structure formation of kaolin. In powdered samples, all cumulative curves split into three groups with different pore volumes. This grouping proves the existence of a dependence of the pore volume on the added amount of humic acid. The lack of proportionality between the total pore volume and the humic acid concentration observed in this study may indicate inhibiting influence of intermediate humic acid doses on flocculation. In pre-wetted kaolin rapid decrease of total pore volume may be explained by the existence of mineral flocculation, even in distilled water.

Lower values of structural parameters were found in compacted samples. The influence of humic acid on compact of kaolin, decreasing with an increase of the amount of humic acid in mineral have been observed.

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REFERENCES

1. **Arora H.S., Coleman N.T.:** The influence of electrolite concentration on flocculation of clay suspensions. Clays a. Clay Miner., 127, 134-139, 1979.
2. **Churchman G.J., Payne D.:** Mercury intrusion porosimetry of some New Zealand soils in relation to clay mineralogy and texture. J. Soil Sci., 34, 437-451, 1983.
3. **Davis J.A.:** Adsorption of natural dissolved organic matter at the oxide/water interface. Geochim. Cosmochim Acta, 46, 2381-2393, 1982.
4. **Diamond S.:** Microstructure and pore structure of impact-compact clays. Clays a. Clay Miner. 19, 239-249, 1971.
5. **Evans L.T., Russell E.W.:** The adsorption of humic and fulvic acids by clays. J. Soil Sci., 10, 119-132, 1959.
6. **Everett D.H.:** Pore systems and their characteristics. In: Characterization of porous solids (Eds K.K. Unger *et al.*). Elsevier Sci. Publish. B. V., Amsterdam 1-21, 1988.
7. **Greenland D.J.**: Interaction between humic and fulvic acids and clays. Soil Sci., 111, 34-41, 1971.
8. **Gorbunov N.I., Yerokhina G.L., Shchurina G.N.:** Relationship between soil minerals and humic substances. Pochvov. 7, 117-128, 1971.
9. **Hajnos M.:** Changes in porosity of soil materials under the influence of flocculants of various ion character. Polish J. Soil Sci., 12, 133-137, 1979.
10. **Hajnos M., Sokolowska Z., Renger M.**: Influence of microrelief and liming on the soil reaction and the microstructure of forest soil (in Polish). Zesz. Probl. Post. Nauk Roln., 1998 (in press).
11. **Ingles O.G.:** Soil chemistry relevant to the engineering behavior of soils. In: Soil mechanics - selected topics .(Ed. I. K. Lee). Elsevier, Y.Y., 1-57, 1968.
12. **Inoue T., Wada K.:** Adsorption of humified clover extracts by various clays. Trans. 9th Inter Congr. Soil Sci., Adelaide, 3, 183-190, 1968.

13. **Jańczuk B., Białopiotrowicz T.:** Components of surface free energy of some clay minerals. Clays a. Clay Miner. 36, 243-248, 1988.
14. **Jekel M.R.:** The stabilization of dispersed mineral particles by adsorption of humic substances. Water Res. 20, 1543-1554, 1986.
15. **Józefaciuk G., Hajnos M., Sokołowska Z., Renger M.:** Influence of surface coverage by humic acids on surface free enerfy and wettability of quartz and kaolin. Polish. J. Soil Sci., 28, 29-35, 1995.
16. **Kodama H., Schnitzer M.:** Adsorption of fulvic acid by non-expanding clay minerals. Trans. 10th Inter, Congr. Soil Sci. Moscow, 2, 51-56, 1974.
17. **Konstankiewicz K., Stawiński J.:** The use of the mercury porosimeter for studies of some soil properties. Polish J. Soil Sci., 17, 45-51, 1976.
18. **Kozak E., Stawiński J., Wierzchoś J.:** Reliability of mercury intrusion porosimetry results for soils. Soil Sci., 152, 405-413, 1991.
19. **Kozak E.:** Methodical aspects of the determination of pores sizes distributions and fractal diameter of soils materials (in Polish). Ph. D. Thesis, Institute of Agrophysics, Lublin, 1994.
20. **Kretzschmar R., Robarge W.P., Weed S.B.:** Flocculation of kaolinitic soil clays: effects of humic substances and iron oxides. Soil Sci. Soc. Am. J., 57, 1277-1283, 1993.
21. **Lawrence G.P.:** Measurement of pore sizes in fine-textured soils: a review of existing techniques. Soil Sci., 28, 527-540, 1977.
22. **Miller W.P., Frenkel H., Newman K.D.:** Flocculation concentration and sodium/calcium exchange of kaolinitic soil clays. Soil Sci. Soc. Am. J., 54, 346-351, 1990.
23. **Murray R.S., Quirk J.P.:** Comments on recent work with critical point dried soils. J. Soil Sci., 32, 161-164, 1981.
24. **Orlov D.S., Pivovarova I.A., Gorbunov N.I.:** Interaction of humic substances with minerals and the nature of their bond. A review. Agrokhimiya, 9, 140-153, 1973.
25. **Ristori G.G., Sparvoli E., Landi L., Martelloni C.:** Microstructure characteristics of two clays soils in relation to clay mineralogy, water content and tillage. Trans. XIII Congr. Inter. Soc. Soil Sci., Hamburg, II, 140-141, 1986.
26. **Schulthess C.P., Huang C.P.:** Humic and fulvic acid adsorption by silicic and aluminum oxide surfaces on clay minerals. Soil Sci. Soc. Am. J., 55, 34-42, 1991.
27. **Sen B.C.:** Studies on the adsorption of humic acid on H-clays and the role of metal cations in humus adsorption. J. Indian Chem Soc., 38, 737-740, 1960.
28. **Sides G., Barden L.:** The microstructure of dispersed and flocculated samples of kaolinite, illite and montmorillonite. Canad. Geotechnic. J., 8, 391-399, 1971.
29. **Sills I.D., Alymore L.A.G., Quirk J.P.:** An analysis of pore size in illite-kaolinite mixtures. J. Soil Sci., 24, 480-490, 1973 a.
30. **Sills I.D., Alymore L.A.G., Quirk J.P.:** A comparison between mercury injection and nitrogen sorption as methods of determining pore size distributions. Proc. Soil Sci. Soc. Am., 37, 535-537, 1973 b.
31. **Sills I.D., Alymore L.A.G., Quirk J.P.:** Relationship between pore size distributions and physical properties of clay soils. Aust. J. Soil Res., 12, 107-117, 1974.
32. **Smalley I.J., Cabrera J.G.:** Particle association in compacted kaolin. Nature 222, 80-81, 1969.
33. **Sokołowska Z., Hajnos M., Józefaciuk G., Hoffmann Ch., Renger M.:** Influence of humic acid on water adsorption characteristics of kaolin and quartz. Z. Pflanzenernahr. Bodenk., 160, 327-331, 1997.
34. **Sokołowska Z., Sokołowski S.:** Influence of humic acid on surface fractal dimension of kaolin: Analysis of mercury porosimetry and water vapour adsorption data. Geoderma, 1998 (in press).
35. **Spark K.M., Wells J.D., Johnson B.B.:** Characteristics of the sorption of humic acid by soil minerals. Aust J. Soil Res. 35, 103-112, 1997.
36. **Swartzen-Allen S.L., Matijevic E.:** Surface and colloid chemistry of clays. Chem. Rev., 74, 385-400, 1974.
37. **Thang B.K.G.:** Formation and properties clay-polymer complexses. Elsevier, 283-314, 1979.
38. **van Olphen H.:** An introduction to clay colloid chemistry. Intersci. Publish. N.Y. 66-242, 1963.
39. **Volzone C., Hipedinger N.:** Mercury porosimetry of compacted clay minerals. Z. Pflanzenernahr. Bodenk., 160, 357-360, 1997.
40. **Wierzchoś J.:** Analysis of physico-chemical conditions of the formation and stability of soil structure (in Polish). Ph.D. Dissertation, IUNG Puławy, 39-44, 1989.