GEOLOGICA CARPATHICA – SERIES CLAYS, 5, 1 – 2, BRATISLAVA, JUNE – DECEMBER 1996
49 – 53

MODIFIED ELECTRODES: SORPTION OF Cu(II) ON MONTMORILLONITE-HUMIC ACID SYSTEM

PETR KULA[1], ZUZANA NAVRÁTILOVÁ[1], MARTA CHMIELOVÁ[1], PETR MARTINEC[1],
ZDENĚK WEISS[2] and ZDENĚK KLIKA[2]

[1]Institute of Geonics, Academy of Sciences of the Czech Republic, Studentská 1768, 708 00 Ostrava, Czech Republic
[2]Technical University Ostrava, Central Analytical Laboratory, 708 33 Ostrava, Czech Republic

(Manuscript received October 1, 1996; accepted in revised form January 14, 1997)

Abstract: Two types of the montmorillonite – humic complex (MMT.HA) were prepared and their sorption properties were studied. X-ray analysis showed changes in the first basal spacing of c-humates prepared by co-coagulation in the comparison with m-humates obtained by mixing and subsequent hydration. Repetitive cyclic voltammetry on the carbon paste electrode modified with MMT.HA proved the influences of sorbed humic acid on Cu(II) sorption onto the MMT.HA.

Key words: clay modified electrode, montmorillonite, humates, copper sorption.

Introduction

Investigation of the clay-humate system and its properties is important because of its significant role in the soil system and in geochemical processes. Recent studies have described the effects of humic substances on the mineralogical and chemical properties of the clay minerals (Buondonno et al. 1989; Singer & Huang 1990). The clay–synthetic humic acid complexes were prepared and studied (Jouany 1991). The humic substances bound onto the clay particles surfaces strongly influence the minerals interactions with hydrophobic organic compounds (Schlautman & Morgan 1993; Murphy et al. 1994). Due to their complexation reactions organic ligands can also change metals sorption onto the clay minerals (Stadler & Schindler 1993). Adsorption of actinides in the system mineral oxide–colloidal humic acid was studied (Righetto et al. 1991). Readsorption and redistribution of the trace metals onto the soil minerals was found in the model soil synthetized from the natural minerals and humic acid (Shan Xiao-Quah & Chen Bin 1993).

Electrodes modified with clay minerals have been exploited in studies of the electrochemical behaviour of redox couples (Bard & Mallouk 1992). The clay modified carbon paste electrodes (CPEs) are successfully employed in the voltammetric analyses (Kalcher 1990), the zeolite modfied CPEs and composite electrodes are suitable for electrochemical studies of zeolite-encapsulated and clay–intercalated metal complexes as biomimetic oxidation catalysts (Bedioui 1995). The clay modified electrodes offer the possibility to contribute to the study of sorption and ion-exchange processes on the clay minerals. The clay saturation with the metals complexes was studied by means of ion exchange voltammetry on the clay film electrode (Fitch 1990). The CPE modified with clay was used as a model system of cations preconcentrating under the open circuit conditions (Kalcher et al. 1995).

The ion exchange reactions of copper(II) with two montmorillonite–humate systems were studied in this work. Voltammetric study of Cu(II) sorption on the montmorillonite by means of CPE modified with this clay mineral was already described (Kula & Navrátilová 1994b). The influences of the humic acids present in the solution on the Cu(II) sorption was found, too (Kula & Navrátilová 1994a). The use of the CPE modified with the montmorillonite–humate system for study of its interactions is a new approach to the research of the clay minerals properties and reactions.

Experimental

Methods

A PA4 Polarographic Analyzer and a Model 4106 X-Y Recorder (Laboratory Instruments, Prague, Czech Republic) were used for voltammetric measurements. An electrochemical cell of conventional design was equipped with a three-electrode system: carbon paste, saturated Ag/AgCl and Pt electrodes. We made our own carbon paste electrode (Navrátilová & Kula 1993). Our measurement procedure

Table 1: Contents of C, H and N in humic acid and in montmorillonite preparations.

Sample	C [%]	H[%]	N[%]
HA	52.370	4.570	0.680
MMT	0.232	1.050	0.011
c-MMT.HA, 1%	0.786	1.550	0.022
c-MMT.HA, 10%	5.750	1.780	0.098
c-MMT.HA, 20%	11.670	2.150	0.169

was as follows: a small piece of the paste was extruded from a plastic tube and removed. The fresh surface was polished on a plastic sheet. The cleaning and polishing procedures were repeated before each measurement. The polished electrode was inserted into the electrochemical cell and the voltammogram was recorded. Repetitive cyclic voltammetry at a scan rate of 20 $mV.s^{-1}$ and at a potential range from -0.6 V to +0.2 V was carried out on the CPE.

X-ray diffraction analysis of the clay samples was performed using a INEL powder diffractometer with a PSD120 position sensitive detector, reflection mode, rotation holder with highly oriented sample, and monochromatized Cu radiation (Ge-monochromator). The first basal diffraction profiles of the clay samples were corrected on the Lorentz-polarization factor and fitted using an asymmetric Pearson 1 profile function.

Spectrophotometry at a wavelength of 400 nm (Specol 10, Carl-Zeiss, Jena) was used for the HA rest determination in the supernatant.

The contents of C, H, N in the preparations (Table 1) were determined by a C, H, N analyzer (EA 1108 Elemental Analyzer, Carlo Erba). The determined C, H and N contents in the c-MMT.HAs corresponds to the values calculated from the HA content in the humate.

Materials and chemicals

Montmorillonite (MMT) Wyoming, USA, was treated by sedimentation of its 1% suspension in redestilled water in order to obtain the fraction below 5 µm. The fraction was air-dried and used for other experiments.

A stock solution of NaHA (2 g/l or 4 g/l) was prepared from a commercial preparation of Na Salt Humic Acid (Serva) (molecular weight M_r = 600 – 1000). Humic acid (HA) was obtained from the solution of NaHA by precipitation with HCl (Navrátilová & Kula 1993).

Sodium acetate and acetic acid (both analytical grade, Merck, Germany) were used for the preparation of the background electrolytes. A stock standard solution of Cu(II) (1 g Cu(II) in 1000 ml) was prepared from Titrisol standard (Merck, Germany). Only redistilled water was used throughout. The glassware was cleaned in a Laborcleaner (Labelchem, Prague) and with distilled water (both for 24 h).

Two types of montmorillonite-humates were prepared.

1. C-humates prepared by co-coagulation (c-MMT.HA).

A proper amount of humic acid (as Na salt solution) was added to a suspension of 500 mg MMT in about 50 ml of water. After diluting the suspension to 100 ml volume, its pH was adjusted to a value of 1.6 by consecutive adding of 30% HCl (analytical grade, Merck, Germany). The suspension was slightly shaken for about 2 min and left quiescent at room temperature. A coagulation and subsequent flocculation occurred after 4 hours. A cleared solution exhibited a value of pH = 2.5 after 24 hours of standing. The montmorillonite-humate complex was centrifuged at 3,000 rpm for 15 min and then it was air-dried. The supernatant was analyzed for humic acid residual content that was not co-coagulated with MMT. The real contents of HA in humates were determined as follows: c-MMT.HA,0.3% (0.3 % HA), c-MMT.HA,1% (1.0 % HA), c-MMT.HA,10% (9.8 % HA) and c-MMT.HA,20% (20.8 % HA).

A blank sample of MMT.HA,0% with a zero content of humic acid was prepared by the same method of co-coagulation. No flocculation was observed after 24 hours of standing, only slight sedimentation of the MMT particles took place. The value of pH increased from the starting value of pH = 1.6 to pH = 3.9.

Solutions of NaHA of the same concentration as used for the clay-humate preparation were treated by the same method in the absence of the clay minerals. No flocculation was observed if these solutions were acidified to pH 1.6.

2. M-humates prepared by mixing (m-MMT.HA).

They were prepared by thorough mixing of the dry MMT with dry solid HA in the proper amount ratio. This mixture was hydrated in an atmosphere saturated with water vapour at room temperature. Weight increase was monitored by weighing. The sample was air-dried after the achievement of the constant weight. Such prepared humates were analysed by X-ray and used for the preparation of the CPEs. Prepared m-montmorillonite-humates contained 0.3 – 10 % of HA (w/w).

Preparation of carbon paste electrodes

Clays are usually suspended in water and the moist suspension is used as a modifier and mixed with the carbon paste (e.g. Wang & Martinez 1989). This method was modified by hydration of the clay or the clay-humate in an atmosphere saturated with water vapour (Kula & Navrátilová 1994a,b). Our own procedure and its advantages are described in more details in the recent publication (Kula & Navrátilová 1996). The same procedure was used for the hydration of the HA modifier, too. The water content in the modifiers is shown in Table 2. The preparations c-MMT.HA,1%, m-MMT.HA,1%, c-MMT.HA,10% and m-MMT.HA,10% were used for the modified CPEs. Apart from these CPEs, CPE(HA) modified with humic acid and unmodified CPE(0) were also prepared. The contents of the modifiers were 10 % in the case of the MMT.HAs and 1 % in the case of HA. The carbon pastes were prepared by thorough mixing of the modifier and carbon powder and by adding of nujol. The detailed procedure for preparation of the CPEs has already been described (Navrátilová & Kula 1993). The geometric area of the electrode was 2.27 mm^2.

Table 2: Water content in the clay preparations used as the CPEs modifiers.

Sample	H_2O [% w/w]
HA	36.0
MMT	24.1
c-MMT.HA, 1%	35.7
c-MMT.HA, 10%	41.9
m-MMT.HA, 1%	24.9
m-MMT.HA, 10%	25.1

Results and discussion

X-ray patterns of montmorillonite-humates

The positions of the maximum (d_{001}) of the first basal diffraction profiles of the MMT and MMT.HAs were evaluated from profiles fitted by the asymmetric Pearson 1 function. The values together with FWHM values are showed in Table 3. The first basal diffraction — d_{001} — of the blank sample (c-MMT.HA,0% obtained by acid treatment in the absence of HA) increased by about 0.5 Å, the FWHM parameter did not change at all. This d_{001} shift can presumably be assigned to rising Al- or hydroxy-Al montmorillonite. Aluminium ions were probably released at the pH below 2.0 and they were subsequently sorbed and hydrolyzed - the resulting pH of the suspension was 3.9.

A further increase of d_{001} (about 1 Å) occurred during the acid coagulation in the presence of a relatively small amount of HA (0.3 %), and the FWHM parameter increased. Both d_{001} and FWHM were not significantly influenced by increasing the amount of HA. The formation of Al- or hydroxy-Al montmorillonite probably continued and deepened during the coagulation and flocculation of the c-MMT.HA complex (reaction of the blank supernatant remained acid — pH = 2.5). The achieved value of d_{001} = 13.482 Å approximates to the value stated for hydroxy-Al montmorillonite (Dubbin et al. 1994). The increased values of FWHM for c-MMT.HAs reflect broader and asymmetric XRD peaks which can be connected with some structural changes in the case of MMT-humates. This fact would be explained by the formation of Al-hydroxypolymers between the clay surface and ligand groups of humic acids. Similar results have also been found in the case of the hydroxy-Al-tannate-montmorillonite complexes (Buondonno et al. 1989).

The m-MMT-humates prepared by simple mixing of the MMT with HA and by subsequent hydration did not exhibit any changes of the first basal diffraction, but the FWHM parameter increased. The structure of m-MMT.HAs does not vary, but moderate changes on its surface can be supposed.

Voltammetric study of Cu(II) sorption

Repetitive cyclic voltammetry (RCV) on the clay CPEs can be used to study clay minerals and their sorption and ion-exchange properties (Fitch 1990; Kula & Navrátilová 1994b). RC voltammograms on the CPE(MMT) show the current increase caused by Cu sorption into the MMT during the cycling of the potential from - 0.6 V to +0.2 V in the electrolyte with Cu(II) (Fig. 1 A). When the current

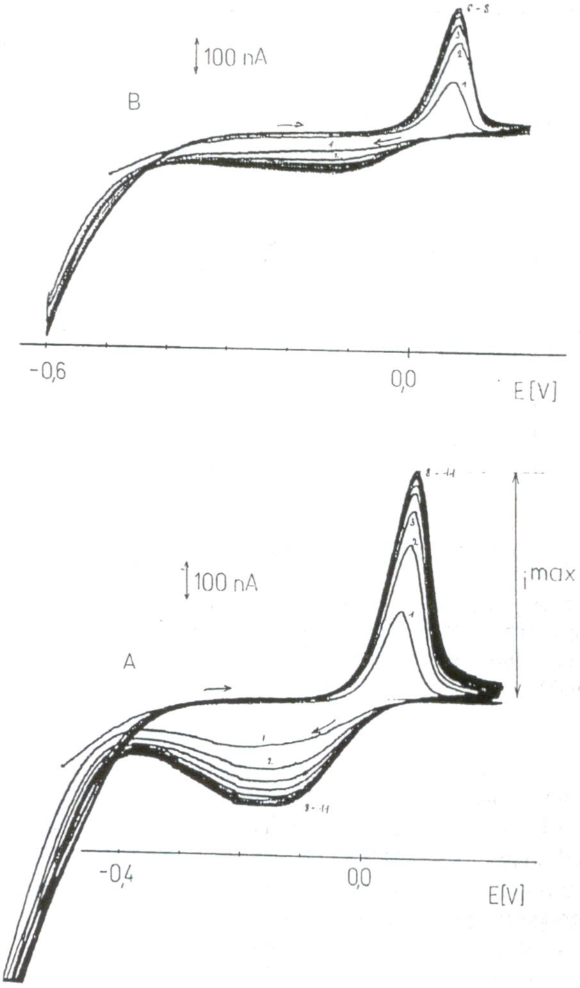

Fig. 1. A— RCV on CPE(MMT), acetate buffer - pH = 3.6, ionic strength I = 0.015 mol, Cu(II) concentration 1 mmol in the cell. **B** — RCV on CPE(c-MMT.HA,10%), conditions as in A.

Table 3: The first basal spacing d_{001} and half-width (FWHM) for the montmorillonite and its humates.

	d_{001} [Å]	FWHM [°2 Θ]
MMT	11.772	1.47
c-MMT.HA,0%	12.330	1.41
c-MMT.HA,0.3%	13.276	2.10
c-MMT.HA,1%	13.042	2.19
c-MMT.HA,10%	13.156	2.12
c-MMT.HA,20%	13.482	2.47
m-MMT.HA,0.3%	11.748	2.23
m-MMT.HA,1%	no measured	
m-MMT.HA,10%	11.768	2.37

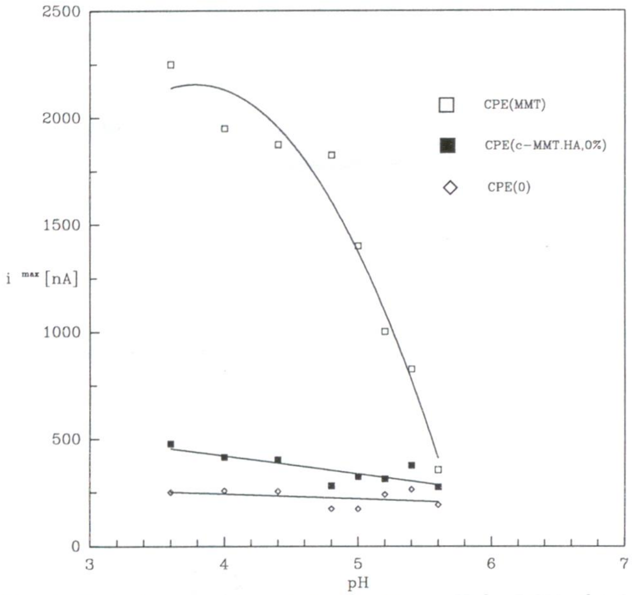

Fig. 2. Dependences of current maximum on pH for RCV of 1.6 mmol Cu(II) on the unmodified and various modified CPEs, background electrolytes - acetate buffer pH 3.6 – 5.6 (non-constant ionic strength).

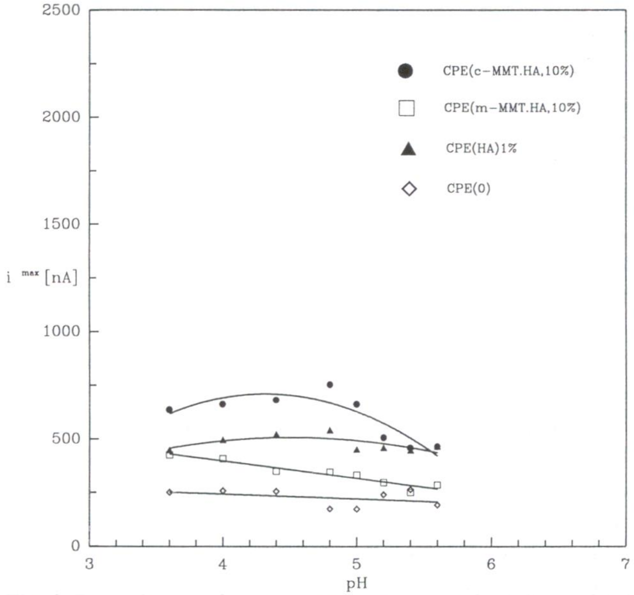

Fig. 3. Dependences of current maximum on pH for RCV of 1.6 mmol Cu(II) on various modified CPEs, background electrolytes - acetate buffer pH 3.6 – 5.6 (non-constant ionic strength) CPE(c-MMT.HA,10%) - 10 % of HA in MMT CPE(m-MMT.HA,10%) - 10 % of HA in MMT CPE(HA)1% - 1 % of HA in paste.

reaches a maximum value, saturation of the ion-exchange sites of the clay is completed. The current response obtained on the CPE(c-MMT.HA,10%) is decreased (Fig. 1,B) and the maximum current is 1.9 times lower than on the CPE(MMT). The maximum current response i^{max} indicates maximum occupation of available ion-exchange sites of the clay by Cu(II) ions in given conditions (pH, Cu(II) concentration in the solution, ionic strength etc.). It is thought, that i^{max} is proportional to the ion-exchange capacity (IEC) of the clay for Cu(II) (Kula & Navrátilová 1994b; Kalcher et al. 1995). The RCV of Cu(II) on the electrodes modified with c-humates and m-humates was measured in dependence on the pH of the solution. The results were compared with the RCV on the CPE(MMT) and CPE(0).

All the measured dependences of i^{max} on pH shown on Figs. 2 and 3 showed a larger or smaller decrease with increasing pH. The most intense decrease was found in the case of the MMT. This course is connected with the initial hydrolysis of Cu(II) ions, therefore with the formation of hydroxycomplexes of Cu(II). The pH range from 3.6 to 4.4 is suitable for the semiquantitative comparison of the obtained dependences, as the Cu(II) hydrolysis does not take place in this pH range. The I^{max} of the c-MMT.HA,0%, therefore its IEC, is four times lower than the IEC of the acid untreated MMT alone in the pH range 3.6 – 4.4 (Fig. 2). However, the i^{max} value for the blank c-humate is twice as high as that for the CPE(0). This suggests, that the IEC of the acidically treated MMT is partly conserved. This finding corresponds qualitatively to the concept on the partial formation of the Al- or hydroxy-Al montmorillonite and so on the non-availability of the larger part of the ion-exchange sites of the MMT.

The i^{max} - pH dependence for the c-humate is similar to the dependence for the HA alone, as it is seen at Fig. 3. This course of the stated dependence shows to the complexation of Cu with HA, as it was already found (Navrátilová & Kula 1993). The i^{max} value for the c-humate is slightly higher than for the HA alone in the pH range 3.6 – 4.4, although the HA content is the same in both electrodes. Also the i^{max} is higher in the case of the c-humate in comparison with blank c-humate (acidically treated MMT). These facts suggest, that both surface of the Al- or hydroxy-Al montmorillonite and HA contribute to the ion-exchange.

The i^{max} - pH dependence for the c-MMT.HA is not the simple sum of the dependences for the blank c-humate (acid treated MMT) and for the HA. This indicates formation of the MMT.HA complex. This presupposition is also supported by the fact, that there is no flocculation at pH = 1.6 in the solution of the alone HA. Thus, it can be supposed, that the c-humate complex is an associate of the folded and aggregated molecules of the HA (pH = 2.5, see Buffle 1988) with part of the surface of the Al- or hydroxy-Al montmorillonite. This idea corresponds to the concept of Chassin 1978.

Fig. 3 shows the dependence i^{max} on the pH for the m-MMT.HA. It is seen, that its IEC significantly decreased in comparison with the MMT alone. Therefore the majority of the ion-exchange sites of the MMT are probably not-available due to nearly complete coating of the MMT surface by the HA molecules. The ion-exchange sites of the HA are exhausted due to their interactions with the MMT surface. A dissociation of the HA functional groups during the hydration of the solid mixture of the MMT and the HA and subsequent bounding with the MMT surface (maybe with

Al atoms) can be supposed. However, a migration of Al ions and formation of Al- or hydroxy-Al montmorillonite did not take place under the conditions of the m-humates preparation. It is shown by the same value of the d_{001} of the m-humates and of the MMT.

Conclusion

The voltammetry on the carbon paste electrodes modified with two types of the montmorillonite-humates and with their components is able to distinguish humates prepared by two different procedures. The possible position of the HA molecules on the MMT particles can be approximately estimated from this measurement.

The supposed structural changes of the montmorillonite during acid co-coagulation with the humic acid are closely connected with effect of Al(III) ions. No structural changes were found in the case of the mixed montmorillonite-humates. However, the presence of the humic acid in this system can alter its surface properties.

The sorption and the ion-exchange reactions of copper (II) with the montmorillonite-humates were found to be dependent on the way they were formed. Positively, the ion-exchange capacity of both montmorillonite-humates is decreased in comparison with the montmorillonite.

The work showed the possibility of utilization of voltammetry with modified carbon paste electrodes for study of the soil system components. Study is in progress in order to find a close description of the clay minerals–humic acid system.

Acknowledgements: We thank Mrs. A. Dušková for technical assistance. The work was supported by the Grant Agency of the Czech Republic, Grant No. 203/93/0363, by the Academy of Sciences of the Czech Republic, Project K. 1042603 and by the project of the European Commission No. CIPD CT925041.

References

Bard A. J. & Mallouk T., 1992: Electrodes modified with clays, zeolites, and related microporous solids. In: R.W.Murray (Ed.): *Molecular Design of Electrode Surfaces. Techniques of Chemistry Series, Vol. XXII. John Wiley & Sons*, Inc. New York., 271–312.

Bedioui F., 1995: Zeolite-encapsulated and clay intercalated metal porphyrin, phthalocyanine and Schiff-base complexes as models for biomimetic oxidation catalysis: and overview. *Coordination Chemistry Reviews,* 144, 39–68.

Buffle J., 1988: Complexation reactions in aquatic systems: an analytical approach. *Ellis Horwood Limited*, Chichester, 1–185.

Buondonno A., Felleca D. & Violante A., 1989: Properties of organominerals complexes formed by different addition sequences of hydroxy-Al, montmorillonite and tannic acid. *Clays and Clay Minerals,* 37, 3, 235–242.

Chassin P., Berre B. & Nakaya N., 1978: Influence des substances humiques sur les proprietes des argiles. *Clay Minerals,* 13, 1–16.

Dubbin W.E., Tee Boon Goh, Oscarson D.W. & Hawthorne F.C., 1994: Properties of hydroxy-Al and -Cr interlayers in montmorillonite. *Clays and Clay Minerals*, 42, 3, 331–336.

Fitch A., 1990: Apparent formal potential shifts in ion exchange voltammetry. *J. Electroanal. Chem.*, 284, 237–244.

Jouany C. L., 1991: Surface free energy components of clay - synthetic humic acid compounds from contact angle measurements. *Clays and Clay Minerals*, 39, 1, 43–49.

Kalcher K., 1990: Chemically modified carbon paste electrodes in voltammetric analysis. *Electroanalysis*, 2, 419–433.

Kalcher K., Grabec I., Raber G., Cai X., Tavcar G. & Ogorevc B., 1995: The vermiculite modified carbon paste electrode as a model system for preconcetrating mono and divalent cations. *J. Electroanal. Chem.*, 386, 149–159.

Kula P. & Navrátilová Z., 1994a: Electrochemical study of Cu sorption onto the clay modified electrodes. *The Proc. of 5th European Conference on Electroanalysis*, Venice, Italy, 1–132.

Kula P. & Navrátilová Z., 1994b: Voltammetric study of clay minerals properties. *Acta Universitatis Carolinae - Geologica*, 38, 2–4, 295–301.

Kula P. & Navrátilová Z., 1996: Voltammetric copper(II) determination with a montmorillonite-modified carbon paste electrode. *Fresenius J. Anal. Chem.*, 354, 5–6, 692–695.

Murphy E. M., Zachara J., Smith S.C., Phillips J.L. & Wietsma T.W., 1994: Interaction of hydrophobic organic compounds with mineral-bound humic substances. *Environmental and Science Technology,* 28, 1291–1299.

Navrátilová Z. & Kula P., 1993: Modified carbon paste electrodes for the study of metal-humic substances complexation. *Anal. Chim. Acta,* 273, 305–311.

Righetto L., Bidoglio G., Azimoti G. & Bellobono I.R., 1991: Competetive actinide interactions in colloidal humic acid - mineral oxide systems. *Environmental and Science Technology*, 25, 1913–1919.

Schlautman M. A. & Morgan J.J., 1993: Binding of a fluorescent hydrophobic organic probe by dissolved humic substances and organically-coated aluminium oxide surfaces. *Environmental and Science Technology*, 27, 2523–2532.

Shan Xiao-Quah & Chen Bin, 1993: Evaluation of sequential extraction for specition of trace metals in model soil containing natural minerals and humic acid. *Anal. Chem.,* 65, 802–807.

Singer A. & Huang P.M., 1990: Effects of humic acid on the crystallization of aluminium hydroxides. *Clays and Clay Minerals*, 38, 1, 47–52.

Stadler M. & Schindler P.W., 1993: The effect of dissolved ligands upon the sorption of Cu(II) by Ca-montmorillonite. *Clays and Clay Minerals,* 41, 6, 680–692.

Wang J. & Martinez T., 1989: Trace analysis at clay-modified carbon paste electrodes. *Electroanalysis*, 1, 167–172.