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Application of Electrochemistry for Studying Sorption Properties of Montmorillonite

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1. Introduction

Electrochemical methods have been used for studying clay minerals to a limited extent in comparison with X-ray diffraction, infrared spectroscopy, thermal analysis etc. However, so called "clay electrodes" have become individual and indisputable part of electrochemistry [1 - 8] since the first electrode modified with clay mineral was described in 1983 [1]. Voltammetry on clay electrodes has found its role in the research of clay minerals and their properties, especially ion-exchange and sorption. A thin layer of inorganic material – clay mineral – on the electrode surface does not possess the significant isolating properties thus charge transport proceeds on the clay electrode. The electrode covered with the clay mineral film enables to study the electrode processes and surfaces. By means of the standard electrochemical methods, transport of charge through the clay layer, the sorption and ion-exchange processes in the clay minerals structure can be studied, too. Accumulation of the electroactive compounds into the clay mineral can be successfully used in electroanalysis [7, 9].

Possibilities of electrochemistry in the study of clay minerals by the clay modified electrodes have been in detail stated in the reviews of A. Fitch and her colleagues [3 - 5]. Very interesting opinion concerning the clay mineral structure is presented in the work dealing with study of flow and transport of compounds through the clay film [5]. The clay structure due to its layers charge forms an electrically charged interphase clay – liquid, thus electric double-layer exists on the surface of the clay minerals particles. The processes taking place in the double-layer are considered to be analogous to those in the interphase electrode – solution. The transport mechanisms in the charged media can be studied by the similar way – for example electroosmosis, electromigration or conductivity. These phenomena study has a practical significance in the electrochemical renewal of the soils contaminated with metals [5], for example the technology for elimination of As, Cu, Cd, Cr, Pb, and Zn from the

localities impacted with the dangerous wastes. Of course, the technology is suitable in the case of the metals ions able to participate in the ions reactions and to migrate. An advantage of the electrochemical removing of metals consists in the low financial costs and the insignificant environmental impact in comparison with the technologies based on extraction vaporization or exhaustion.

Cyclic voltammetry on the clay modified electrodes has been used to study the sorption properties of clay minerals. Repetitive (multisweep) cyclic voltammetry on the clay modified electrode exhibited dependences similar to the sorption isotherms [8]. A consecutive occupation of the ion-exchange sites in the structure of clay mineral by an appropriate compound results in a potential shift in comparison with the unmodified electrode. With increasing concentration of sorbate the potential shift exhibits curves in the shape of the sorption isotherms which can be used to evaluation of an extent of the ion-exchange or sorption process. Sorption of metals cations on montmorillonite, vermiculite and kaolinite was studied by means of multisweep cyclic voltammetry on the carbon paste electrodes modified with these clays [10]. Similarly to [8] the current response dependences on the cycling time exhibited the same course as the sorption isotherms. The dependences enable to distinguish an extent of sorption of the individual cation and an ability of clay mineral to adsorb the given cation, of course only in the first approximation. For example, the highest sorption of copper was found in the case of montmorillonite, which was used for determination of Cu [11]. The current vs. time dependences obtained by multisweep cyclic voltammetry on the montmorillonite modified carbon paste electrodes were used for determination of the Cu(II) adsorption kinetics [12]. Adsorption of Cu(II) on the various types of montmorillonite was found to be in accordance with the second order model, the experimental values of the maximum current correlate to those calculated from the supposed equation of the kinetics. Cation exchange of Ag(I) and Ca(II) studied on the carbon paste electrode modified with vermiculite showed to be a dominant process of the cations sorption; the simplified model was worked out and equilibrium constant of the Ag(I) ion exchange was determined [13]. The equilibrium constant value was in a good agreement with the constant determined by other method.

In spite of the lower anion exchange capacity of clay minerals in comparison with the cation exchange capacity the exchange of the complex anions $[Hg(ac)_4]^{2-}$, $[HgCl_4]^{2-}$, and $[HgCl_3]^-$ (ac – acetate) was proved on the carbon paste electrodes modified with montmorillonite and vermiculite [14] and it was used for determination of Hg [15]. The same mechanism was found in the case of $[Au(Cl)_4]^-$ on the montmorillonite modified carbon paste electrode [16], which was also used in the electroanalysis [16, 17]. The lower anion exchange ability of clay minerals is caused by presence of the negative charge of layer. It is supposed, that the anion forms of compounds are "repelled" and they are not gripped in the interlayer [4]. A suitable chemical modification of clay minerals can enhance their affinity to anions. This so called "tunning charge selectivity" has been applied in the field of clay electrodes [18]. For example, smectite with bound propylamine groups exhibited the higher ability to accumulate anion $[Fe(CN)_6]^{3-}$ due to protonization of amine groups. The originally cation-exchange smectite was "tunned" to anion-exchange.

Clay minerals represent the significant natural matrix in the soil medium, which participate in many geochemical processes both natural and those connected with transport and behaviour of the anthropogenic compounds in the soils. Interactions of clay minerals with metal and organic compounds influence their activity, transport, and biological availability. The electrodes modified with clay minerals can serve as a model suitable to study some soil processes connected with clay minerals. The carbon paste electrode modified with vermiculite was used as a model of soil fraction to study the binding interactions of Cu(II) with vermiculite [19]. The selected pesticides and their influence on sorption of Cu(II) on vermiculite were studied. The noncomplexing ligands such as fenamiphos, fenmedipham, and atrazine did not exhibited any influence on the Cu(II) ions sorption. The compounds such as desethylatrazine, desizopropylatrazine, and desethyldesizopropylatrazine do not bind on vermiculite, but they decrease the Cu(II) sorption due to formation the coordination compounds with Cu(II). Apart from the determination of these influences on the metal sorption on clay mineral kinetic and thermodynamic aspects of the sorption processes can be characterized by this way. A soil organo-clay complex – clay humate – is formed by interaction of natural organic matter based on humic and fulvic acids with the clay particles surfaces. The humic adsorbates significantly change properties of clay minerals which influenced their reactions with both natural and anthropogenic substances. The carbon paste electrode modified with the prepared clay humates was used for characterization of the clay minerals reactions with Cu(II) in comparison with the origin clay minerals [20]. Cyclic voltammetry on these electrodes distinguished various types of the clay humates, the obtained results were proved by X-ray diffraction study of the clay humate structures.

Organo-clay modified electrodes represent a new type of clay modified electrodes similar to those with clays grafted with the suitable organic function groups [18, 21, 22]. Similarly as the above mentioned "tunning charge selectivity", cation-exchange ability of clay can be changed to anion-exchange ability due to the cationic surfactants adsorbed onto the clay structure [23]. Clay minerals intercalated with alkylammonium cations (cationic surfactants) exhibit the higher affinity to organic compounds. For example, montmorillonite intercalated with hexadecyltrimethylammonium as a modifier in the carbon paste electrode was able to adsorb pesticides isoproturon, carbendiazim, and methyl parathion [24], which showed to be suitable for stripping voltammetric determination of these pesticides in soil and water. Preconcentration of phenol on glassy carbon electrode modified with film of hydrotalcite-like clay containing surfactant sodium octyl sulfate, sodium dodecyl sulfate, or sodium dodecylbenzenesulfonate [25] as well as octylphenoxypolyethoxyethanol or cetylpyridinium bromide [26] was studied. The electrodes exhibited good sensitivity and reproducibility of phenol determination [25]. Carbon paste electrode modified with montmorillonite exchanged with hexadecyltrimethylammonium bromide was successfully used to determine 4-chlorphenol in water samples [27]. Sorption of Hg, Cd, Pb, Cu, and Zn on montmorillonite intercalated with hexadecyltrimethylammonium cations resulted in use of this organo-montmorillonite as a carbon paste modifier [28]. This organo-montmorillonite loaded with 1,3,4-thiadiazole-2,5-dithiol exhibited an excellent selectivity for Hg(II) ions in presence of other ions. The carbon paste electrode modified with these 1,3,4-thiadiazole-2,5-dithiol-organo-montmorillonite provides a selective sensor for the mercury determination.

The examples mentioned above have at least one common denominator: processes are accompanied by changes of charge on or inside materials. The measurement of zeta potential is one of the methods which provide to obtain imagination about character of the particle surface itself and then also about the processes running on this surface (e.g. adsorption, ion exchange, modification). The experiments connected to the zeta potential measuring represent a factor helping to explain the principles of interactions between surface and its surroundings. As an example heavy metals adsorption on clay minerals (heavy metals removing) or surfactant adsorption on carbonaceous materials (flotation of coals) can be mentioned. The zeta potential knowledge can be also applied in the field of oxidative catalysts, pigments, waste slurries, etc. [29 – 31].

Clay minerals are very often characterized by measurement of the zeta potential. One of the most common measurements is monitoring the zeta potential changes with changing the pH value. This monitoring is performed by titration of montmorillonite, illite, and chlorite by hydrochloric acid and sodium hydroxide. The dependence of the zeta potential on pH exhibited a typical form. The acid addition led to increase of the zeta potential, on the contrary increase in pH (addition of base) caused decrease of the zeta potential. The individual clay minerals exhibited differences arising from the structure and chemical composition of the studied samples. The most significant change of pH came up in the case of chlorite and it was also the only one clay mineral where the isoelectric point was determined (pH=5) [32]. Knowledge of the zeta potential value at the given pH is necessary for understanding the processes running on the surfaces.

The adsorption of heavy metals and metal oxides on the surface of clay minerals plays an important role as well. Sorption of iron and aluminium on the surface of illite, montmorillonite and kaolinite led to reduction of the negative charges on the particle surface so that the isoelectric point of these minerals was shifted to the higher values of pH [33].

The zeta potential of zeolites was examined in connection to the sorption of heavy metals on these adsorption materials. Dependence of the zeta potential on pH was influenced by concentration of a bulk electrolyte ($NaNO_3$). As the concentration of $NaNO_3$ was increasing the value of the zeta potential was increasing as well. That fact is explained by change of thickness of double-layer caused by ionic strength of solution. These changes consequently influenced the adsorption of heavy metals (Pb, Cu, Cd, and Zn). The highest adsorption capacity was found in water [34].

The surfactant molecules generally adsorb in the interfaces between two bulk phases such as solid-liquid or electrode-solution [35]. When adsorbing on solid an ionic surfactant exhibits the surface charge. Zeta potential is one of few effective techniques for characterization of the surface charge as well as the surface chemical properties of solids in solution and for understanding the changes on the solid surfaces. The zeta potential values correspond to the quantity and quality of functional groups on the surface [36].

The work deals with use of the montmorillonite modified carbon paste electrodes for studying of the Cu(II) sorption on two types of montmorillonite - montmorillonite SAz-1

and montmorillonite SWy-2 - and their organo-derivatives containing alkylammonium cations - hexadecyltrimethylammonium, benzyldimethylhexadecylammonium, and hexadecylpyridinium. The zeta potential measurement was used to characterize the Cu(II) and hexadecyltrimethylammonium cation sorption on montmorillonite.

2. Experimental part

2.1. Materials and chemicals

Montmorillonites of two types – montmorillonite SAz-1 (MMT,SAz-1) (Apache County, USA) and montmorillonite SWy-2 – (MMT,SWy-2) (Crook County, USA) were provided from The Clay Minerals Society, Source Clays Repository (USA). The fraction used for all experiments consisted of 80 % of particles below 5 μm (Fritsch Particle Sizer Analysette 22, Fritsch GmbH, Idar-Oberstein, Germany). Another sample of montmorillonite MMT,Wy (deposit Wyoming) was obtained from an older collection of colleagues from Institute of Geonics, CAS Ostrava.

Cation exchange capacity (CEC) was calculated as the sum of cations exchanged with NH_4^+ ions during leaching per gram of montmorillonite [14]. The CEC values were 56 cmol(+)/kg and 76 cmol(+)/kg for MMT,SAz-1, resp. MMT,SWy-2. Mineralogical characterisation was performed by infrared spectrometry and X-ray diffraction [37]. The montmorillonite samples were classified as pure montmorillonites without any admixture of other minerals including quartz.

Organo-montmorillonites were prepared by intercalation of three alkylammonium cations. Hexadecyltrimethylammonium bromide (HDTMABr) (Sigma-Aldrich), benzyldimethyl hexadecylammonium chloride (BDHDACl) (Fluka), and hexadecylpyridinium bromide (HDPBr) (Sigma-Aldrich) of analytical reagent grade were used to prepare the modified montmorillonites MMT,SAz-1–HDTMA, MMT,SAz-1-BDHDA, MMT,SAz-1-HDP), MMT,SWy-2–HDTMA, MMT,SWy-2-BDHDA, MMT,SWy-2-HDP.
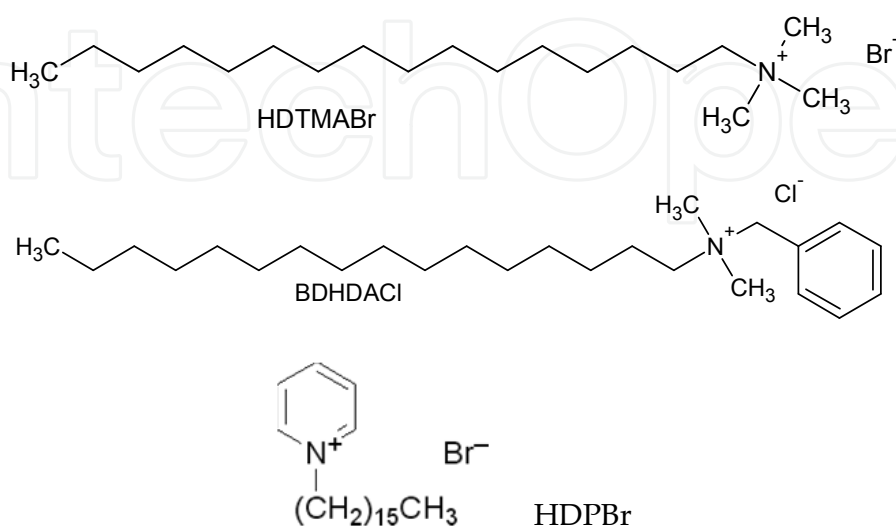
Figure 1. Structures of the used alkylammonium cations

All the chemicals used (sodium acetate and acetic acid for preparation of the background electrolyte as well as sodium hydroxide and hydrochloric acid for measurement of zeta potential) were of analytical grade (Merck, Darmstadt, Germany). The sorption solutions of copper were prepared from $Cu(NO_3)_2 \cdot 3H_2O$ (Lachema Neratovice). The Cu standard for AAS (Cu) (Fluka) was used for AAS analysis. Stock standard solutions of Cu for voltammetry were prepared from Titrisol standards (Merck, Darmstadt, Germany).

3. Procedures

3.1. Preparation of carbon paste electrodes

Carbon paste electrodes (CPEs) modified with either montmorillonites or their organo-derivatives were prepared by the standard procedure [7]. Flake graphite and paraffin oil (Nujol) were thoroughly mixed; in the case of the modified CPEs, an appropriate amount of modifier was added to the graphite before mixing it with oil. A ratio of graphite or the admixture of graphite–modifier to oil was 2.5. The modifier content in the prepared carbon pastes was 10 %, (w/w). The electrodes modifier was before mixing to the carbon paste previously saturated with water vapour, which ensured that the modifier was sufficiently wet but without excess water. No activation and regeneration of the electrode surface prepared in such a way was necessary. The surface was easily renewed by extruding a very small amount of paste and by polishing it on a plastic sheet or scratchboard.

The following carbon paste electrodes were prepared:

-    CPE(0) – unmodified carbon paste electrode
-    CPE(MMT,SAz-1) – carbon paste electrode modified with 10 wt.% (mass %) of montmorillonite SAz-1
-    CPE(MMT,SAz-1-HDTMA) – carbon paste electrode modified with 10 wt.% (mass %) of HDTMA-montmorillonite SAz-1
-    CPE(MMT,SAz-1-BDHDA) – carbon paste electrode modified with 10 wt.% (mass %) of BDHDA-montmorillonite SAz-1
-    CPE(MMT,SAz-1-HDP) – carbon paste electrode modified with 10 wt.% (mass %) of HDP-montmorillonite SAz-1
-    CPE(MMT,SWy-2) – carbon paste electrode modified with 10 wt.% (mass %) of montmorillonite MMT,SWy-2
-    CPE(MMT,SWy-2-HDTMA) – carbon paste electrode modified with 10 wt.% (mass %) of HDTMA-montmorillonite SWy-2
-    CPE(MMT,SWy-2-BDHDA) – carbon paste electrode modified with 10 wt.% (mass %) of BDHDA-montmorillonite SWY-2
-    CPE(MMT,SWy-2-HDP) – carbon paste electrode modified with 10 wt.% (mass %) of HDP-montmorillonite SWy-2

3.2. Cyclic voltammetry

Multisweep cyclic voltammetry (MCV) on the modified CPEs was performed on EKO-TRIBO-Polarograph (EKOTREND, Prague, Czech Republic). A three-electrode cell was

equipped with a carbon paste electrode (CPE) (working), an Ag/AgCl (saturated KCl) reference electrode, and a Pt wire auxiliary electrode. MCV at a scan rate of 20 mV s^{-1} was applied with a potential range from –0.6 V to +0.2 V.

3.3. Sorption of copper

An appropriate amount of montmorillonite or its organo-derivative and a volume of the Cu(II) solution (concentrations in the range 0,5 – 10 mmol . l^{-1}) was inserted into an Erlenmeyer flask (ratio solid : liquid = 1 : 100). The suspension was shaken at the laboratory temperature for 24 h. The amount of the adsorbed Cu(II) was determined as a difference between its concentration before and after the sorption (equation 2 below).

3.4. Zeta potential measurement

The Coulter Delsa 440 SX (Coulter Electronic, USA) instrument was used to measure the zeta potential. Delsa 440 SX uses the scattering effect of Doppler light to determine the electrophoretic mobility. The zeta potential was obtained from the electrophoretic mobility by the Smoluchowski equation:

$$\zeta = \frac{\mu.\eta}{\varepsilon} \tag{1}$$

ζ is the zeta potential (V), η represents dynamic viscosity (Pa.s), and ε stands for the dielectric constant. The fixed conditions of measuring were the following ones: temperature (298 K), electric field (15 V), frequency (500 Hz), and the properties of the samples – viscosity (0.0089 kg.m^{-1}.s^{-1}), refraction index (1.333), and dielectric constant (78.36). The samples were sonicated for 1 minute before zeta potential analysis. All zeta potential measurements were at least duplicated; the mean relative standard deviation of the values reported usually did not exceed 5 %. All the solutions were made in distilled water. Analytical grade chemicals were used. Zeta potential measurements consisted from three steps.

At first a dependence of zeta potential on pH was measured. An amount of 0.1g montmorillonite MMT,Wy was added to the flask with 50 ml of distilled water. The pH value of each suspension was adjusted by adding either NaOH or HCl; pH of the solution was measured using the combination single-junction pH electrode with Ag/AgCl reference cell (LP Prague, model MS 22 pH meter).

The second and the third step of the zeta potential measurements were in principle the same. The zeta potential changes were monitored after adsorption of Cu(II) and HDTMA on MMT,Wy. The clay fraction with the particle size below 5 μm was used for the adsorption experiments. The clay amount of 0.1 g of was weighed in the flask and 100 ml of the Cu(II) or HDTMA solution of a known concentration was added. The suspensions were inserted into a thermostatic bath (25°C) and flasks were permanently shaken. As it was found in the previous experiments, a 24 hours′ period is needed to reach equilibrium. The zeta potential

of the adsorption suspensions was measured. Then, the clay sample was separated by filtration with paper filter.

The amount of Cu(II) and HDTMA adsorbed (*a*) was determined from the change in the solution concentration before and after equilibrium, according to:

$$a = \frac{(c_0 - c_e)V}{m} \tag{2}$$

where c_0 is the initial concentration of the HDTMA solution, c_e the concentration of the HDTMA solution at the adsorption equilibrium, *V* the volume of the HDTMA solution and *m* the mass of the clay.

The HDTMA concentration of the filtered solutions was determined by UV/VIS spectrophotometry (ALS laboratory group, CZ_SOP_D06_07_N03).

3.5. Preparation of organo-montmorillonites

An amount of 1 g of montmorillonite and 100 ml 7.5 mmol . l^{-1} solution of alkylammonium cation was shaken at the laboratory temperature for 2.5 h (the time was found in the previous experiments). After the sorption the suspension was centrifuged (9000 rev min^{-1}) for 10 min. The supernatant was removed, the solid was washed out with 5 ml solution of ethanol : water = 2 : 1 and the suspension was again centrifuged at the same rate. The washing out was repeated with 5 ml of ethanol and the preparative of organo-montmorillonite was air dried after centrifugation.

3.6. X-ray diffraction

X-Ray diffraction (XRD) was carried out at Nanotechnology Centre, VSB-Technical University Ostrava. XRD patterns of the tested samples were measured by diffractometer INEL equipped with Cu anode, generator (2000 sec, 35 kV, 20 mA) and detector CPSD 120, samples were measured in a flat rotation holder.

3.7. Infrared spectroscopy

Infrared spectra were recorded on Nicolet Avatar 320 FTIR spectrometer (ThermoNicolet, USA) equipped with the DTGS/KBr detector for the middle IR range. The KBr pressed-disc (13 mm diameter) technique (1 mg of sample and 200 mg of KBr) was used. The spectra were measured in the spectral range from 4000 to 400 cm^{-1} (64 scans, 4 cm^{-1} resolutions).

3.8. Thermal analysis

Thermal analysis was carried out using multimodular thermal analyser SETSYS 12-SETARAM equipped with a measurement head TG/DTA rod (Institute of Geonics, CAS, Ostrava). The TG/DTA curves were recorded under an air environment from 25 to 1200 °C, the heating rate was 10 K min^{-1}.

3.9. Analysis of metals

The metal amount in the supernatant after sorption was found by means of atomic absorption spectrometry (AA240FS Varian, USA) by flame atomization air-acetylene (flow rate 13.5 l min^{-1}, λ_{Cu} 249.2 nm, and slit width 0.5 nm for Cu.

3.10. Analysis of alkylammonium cations

The HDTMA concentrations in the supernatant after sorption were determined by UV-VIS spectrophotometry (ALS laboratory group, CZ_SOP_D06_07_N03, Ostrava, Czech Republic). The BDHDA and HDP concentrations in the supernatant after sorption were determined by UV VIS spectrophotometry (Varian Cary 50) at 264 nm (BDHDA) and 260 nm (HDP). The amount of the adsorbed metal was determined as a difference between its concentration before and after the sorption. The amount of the adsorbed alkylammonium cation was determined as a difference between its concentration before and after the sorption (equation 2).

4. Results

4.1. Characterization of prepared organo-montmorillonites

The obtained XRD patterns of the organo-montmorillonites were analysed for d-values of the basal spacing (001) and compared with those of the original montmorillonites (Table 1).
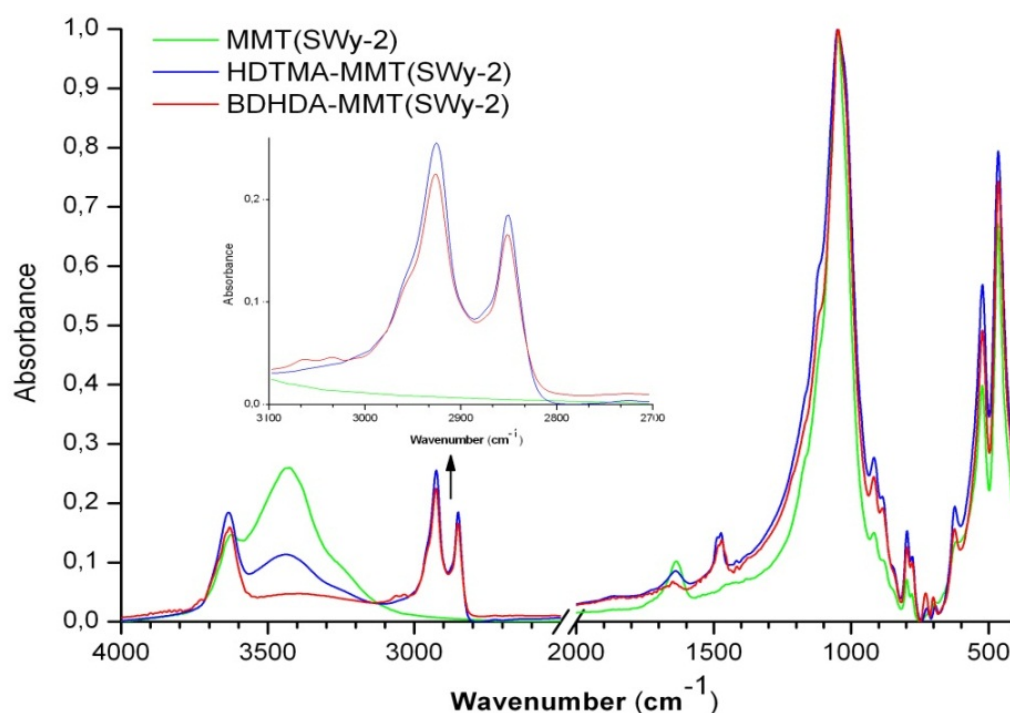
montmorillonite	d(001) [nm]	montmorillonite	d(001) [nm]
MMT,SAz-1	1.47	MMT,SWy-2	1.36
MMT,SAz-1–HDTMA	1.65	MMT,SWy-2–HDTMA	1.68 – 2.40
MMT,SAz-1–BDHDA	1.78 – 2.40	MMT,SWy-2–BDHDA	1.79
MMT,SAz-1–HDP	1.69 – 2.20	MMT,SWy-2–HDP	1.72

Table 1. Basal spacing values d(001)

The organo-montmorillonites exhibited an evident increase of the basal spacing in comparison with those of the unmodified which indicates an intercalation of alkylammonium cations in their interlayer [38 - 40]. The obtained values about 1.7 nm can be judged to bilayer arrangement of cations, the higher values about 2.2 – 2.4 nm probably correspond to a paraffin-type of arrangement – the ammonium groups are attached to the silicate layer, the nonopolar chains are oriented under the tilt angle [41, 42].

The infrared spectra of the original montmorillonites have been already studied [37] and interpreted according to [43]. The infrared spectra of the organo-montmorillonites were interpreted with help of the spectra of the pure alkylammonium salts to distinguish new absorption bands in the organo-montmorillonites. All infrared spectra exhibited characteristic absorption bands of the presented alkylammonium cations. The absorption bands at 2920 cm^{-1} correspond to antisymmetric stretching vibrations and the bands at 2850

cm^{-1} to symmetric stretching vibrations of C – H bounds reflecting alkyl chains of alkylammonium cations. The presence of benzene ring in BDHDA and HDP is confirmed by symmetric stretching vibration of C – H bounds in aromates at 3050 cm^{-1} and by symmetric stretching vibration of C – C bounds of conjugated system at 1620 and 1471 cm^{-1}. The absorption band at 1487 cm^{-1} corresponds to bending vibration of the N – H bounds of ammonium groups. The measured infrared spectra of MMT,SWy-2 and its derivatives with HDTMA and BDHDA are shown at Figure 2. The other organo-montmorillonites exhibited the similar infrared spectra. The presence of all cations in the organo-montmorillonites is evident due to either intercalation or adsorption process.

Figure 2. Infrared spectra of montmorillonite SWy-2 and its organo-derivatives

Thermogravimetric (TG) and differential thermal (DTA) curves of the original montmorillonites were found in the curve library of Clay Minerals (Institute of Geonics, CAS, Ostrava). The peak temperatures for montmorillonites obtained from DTA curve are: 166 °C and 234 °C for dehydration, 673 °C and 884 °C for dehydroxilation/melting and 1027 °C for recrystallization/transformation. In the case of the organo-montmorillonites, the shape of TG/DTA curves corresponded to the original montmorillonites, but the thermal effects exhibited the slightly different temperatures and intensities. The organo-montmorillonites exhibited the higher values of temperatures related to the total melting. The temperatures of exothermic effects connected to recrystallization and transformation increased with the increasing amount of the alkylammonium cations. The temperature and intensity of the first two peaks related to the dehydration process decreased with the

increasing amount of the added surfactant. In addition, the organo-montmorillonites are subjected to a thermal effect at the temperature interval 270–450 °C corresponding to the alkylammonium decomposition [44]. As expected, the mass loss in the whole temperature interval 25-1200 °C increased with increasing amount of the alkylammonium cations.

The results obtained by X-ray diffraction, infrared spectroscopy and thermal analysis proved the presence of the alkylammonium cations in the organo-montmorillonites. As it was already stated [38, 45] intercalation of alkylammonium cations takes place due to both ion-exchange and induced and π-π interactions forming a double-layer in the interlayer space of montmorillonites. Although the previous work [38] supposed the higher intercalation due to a content of benzene ring in the case of BDHDA, the values of the parameter d(001) (Table 1) do not prove this suggestion.

4.2. Characterization of montmorillonite by zeta potential measurement

4.2.1. The pH influence on zeta potential of montmorillonite suspension

The most important factor that affects the zeta potential is pH. The zeta potential value on its own without a stated pH is only a virtually meaningless number. Generally, the zeta potential versus pH curve will be positive at low pH and lower or negative at high pH. The point where the plot passes through the zero value of the zeta potential is called the isoelectric point and it is very important from a practical consideration. It is normally the point where the colloidal system is stable to a lesser extent.

The following figure shows a typical curve for the zeta potential value on the pH value in the case of the montmorillonite particles.
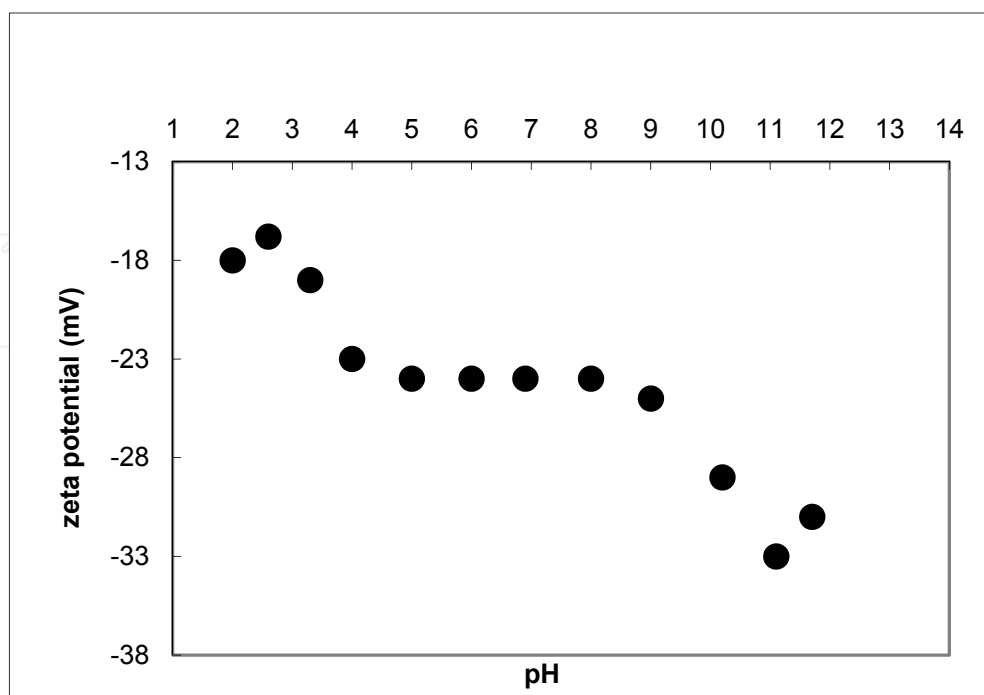

Figure 3. The influence of pH on zeta potential of the MMT,Wy particles

The zeta potential of the montmorillonite particles in distilled water (pH 6) reaches approximately -24 mV, the zeta potential is negative. With increasing addition of alkali to the suspension of pH 6 the particles tends to acquire a more negative charge and with increasing addition of acid a charge is negative to a lesser extent.

At least two main results can be mentioned from the previous picture:

- the zeta potential of the montmorillonite particles did not change significantly in the pH range 4 - 9. In this range particles have tendency to coagulate.
- in the strongly acid solution the zeta potential became positive but the isoelectric point was not reached.

Next, the zeta potential of the montmorillonite particles in the copper solutions was determined during the Cu(II) sorption. The values of the zeta potential before and after the Cu(II) adsorption on the montmorillonite were compared (Figure 4).
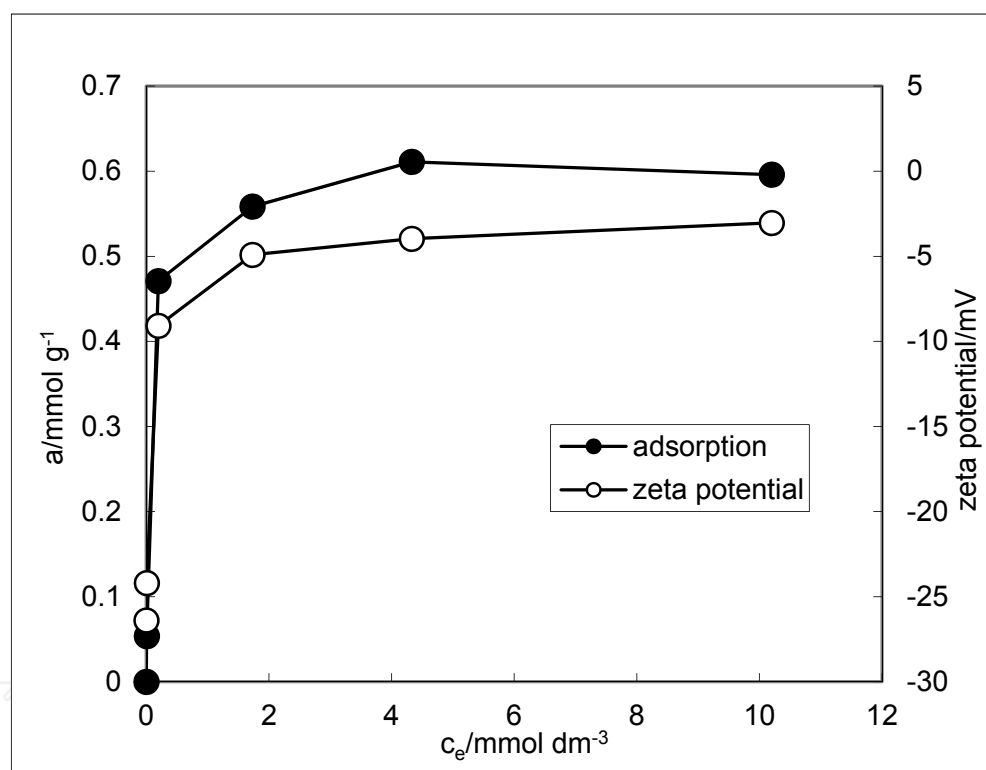
Figure 4. Figure 4. Dependence of zeta potential and adsorption of Cu(II) on MMT,Wy on the Cu(II) equilibrium concentration (c_e)

The adsorption of the copper ions caused the change of the zeta potential of the clay particles. The zeta potential became more positive. On the contrary to Figure 3 where the isoelectric point was not reached with increasing H^+, in the case of addition of the cooper ions the zeta potential was very close to 0 mV. It just confirmed well known fact that the valencies of the ions have great impact on the electrokinetic behaviour of the suspensions.

The zeta potential changes during the Cu(II) sorption can be used as an additional parameter for characterization of the sorption on montmorillonite. The excellent correlation

of the Cu(II) adsorption isotherm with the zeta potential dependence on the Cu(II) concentration in the sorption solutions demonstrated on Figure 4 proved this conclusion.

4.2.2. Sorption of alkylammonium cations – coherence of classical batch experiments and zeta potential measurement

The following research has been performed in order to show the above mentioned possibility of zeta potential for evaluation of the sorption processes. The adsorption of HDTMA on the montmorillonite SAz-1 was studied by conventionally measured adsorption isotherms and the zeta potential was measured simultaneously in the sorption suspensions. Figure 5 demonstrates the typical adsorption isotherm which shape indicates the adsorption isotherm of Langmuir model of monolayer coverage of an adsorbent.
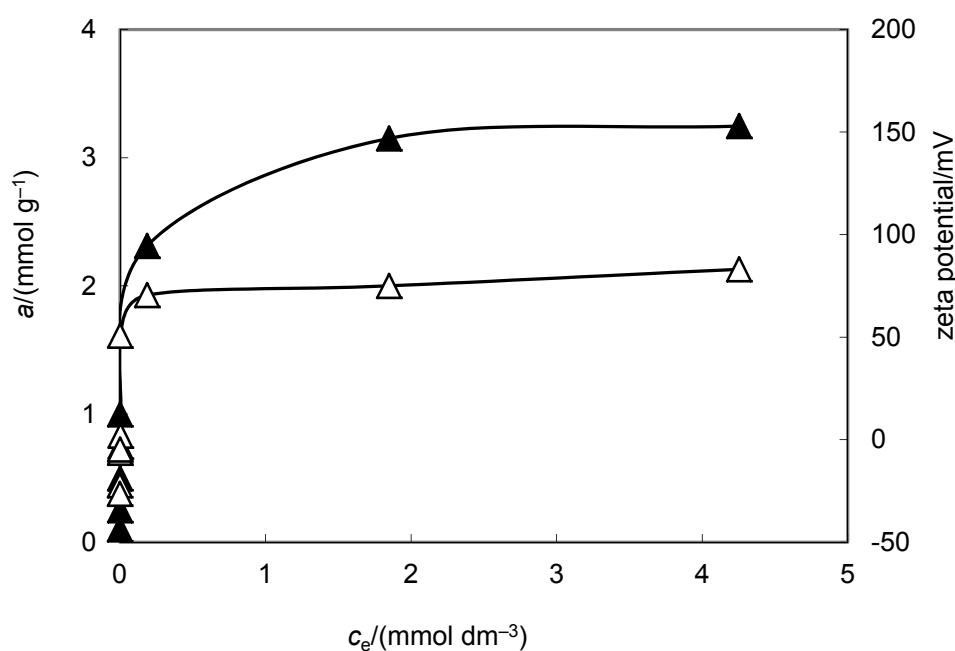
Figure 5. Dependence of zeta potential (blank symbols) and adsorption of HDTM (full symbols) on MMT,SAz-1 on the equilibrium concentration of the HDTMA solution (c_e) [45]

Figure 5 shows the remarkable same course of the adsorption isotherm and the changes of zeta potential of the adsorption system indicating a change of the surface charge due to the HDTMA adsorption. In comparison to other studied sorbent (e.g. coal), the zeta potential is influenced by adsorption to a lesser extent on montmorillonite (about 100 mV). However, an amount of the adsorbed HDTMA is much more higher on montmorillonite and it even exceeds its cation exchange capacity, which proves the concept of the double- or triple-layer arrangement of the adsorbed alkylammonium cations. Thus, adsorption of HDTMA on montmorillonite probably takes place by cation exchange into its interlayer space as well on the external surface. Subsequently, the HDTMA adsorption proceeds via van der Waals interactions [45].

4.3. Comparison of Cu(II) sorption on montmorillonites and their organo-derivatives

4.3.1. Batch technique study

The adsorption isotherms of Cu(II) measured by the batch technique on montmorillonites and their alkylammonium-derivatives are demonstrated on Figures 6 and 7. It is evident that the presence of all three alkylammonium cations in the montmorillonites caused a decrease of the Cu(II) sorption. No significant differences were found in the case of individual alkylammonium cation, the sorption was decreased on about 50 % in comparison with the original montmorillonites. The same decrease of sorption was also found in the case of HDTMA [46] and tetrabutylammonium cations [47]. The sorption sites of clay mineral are occupied by a relatively great alkylammonium cation, which inhibits sorption of the metal cations.
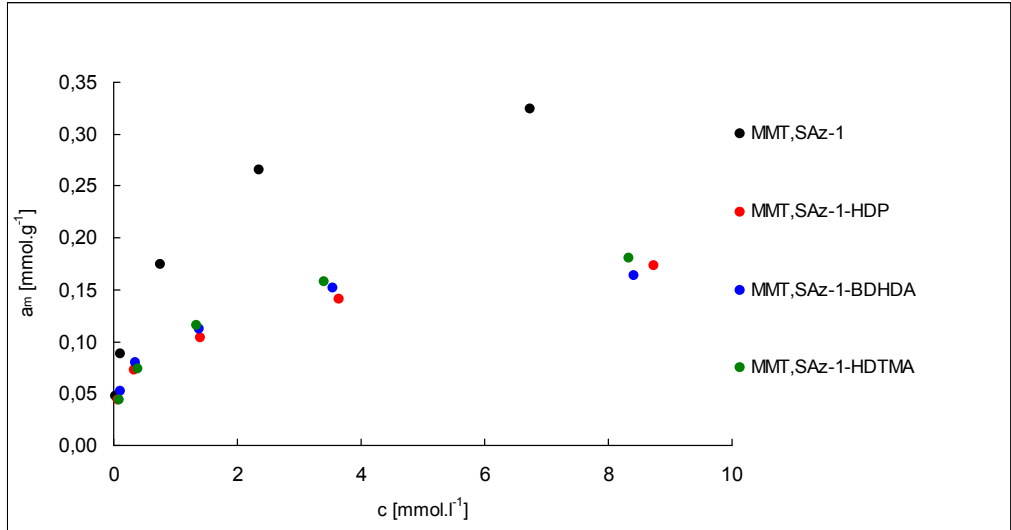
Figure 6. Adsorption isotherms of Cu(II) on MMTA,SAz-1 and its organo-derivatives
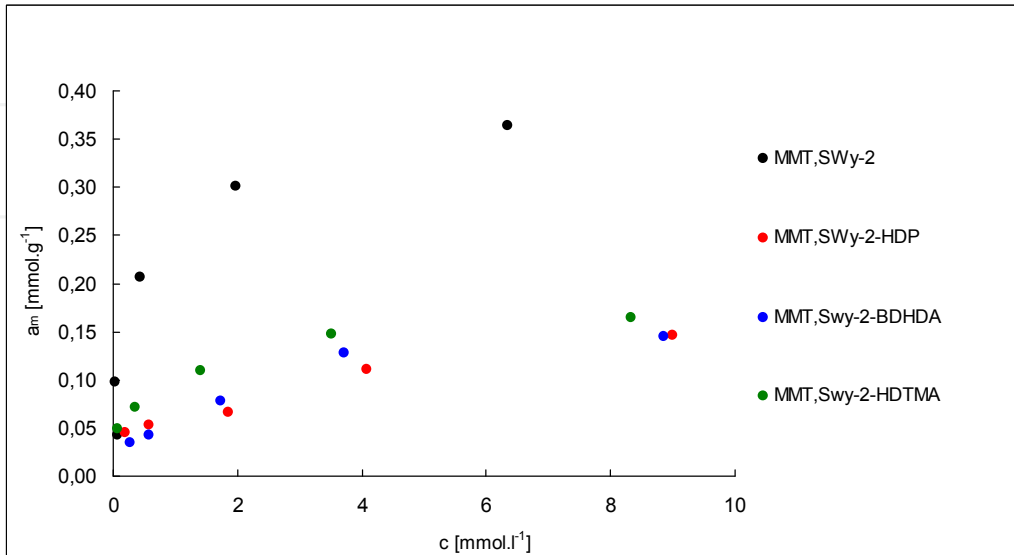
Figure 7. Adsorption isotherms of Cu(II) on MMTA,SWy-2 and its organo-derivatives

The linearized forms of the adsorption isotherms proved that all obtained adsorption isotherms exhibited the Langmuir model of sorption. The linearized forms of the adsorption isotherms were used to calculate a maximum adsorbed amount of Cu(II) named a_{Cu} (Table 2). The values of parameter a_{Cu} indicate no significant differences between the studied organo-montmorillonites. This fact corresponds to the found changes of the parameter d(001) that indicated very similar increase of the basal spacing in all prepared organo-montmorillonites (Table 1).

| Montmorillonite	a_{Cu} [mmol . g^{-1}]	montmorillonite	a_{Cu} [mmol . g^{-1}]
MMT,SAz-1	0.34	MMT,Swy-2	0.38
MMT,SAz-1–HDTMA	0.17	MMT,Swy-2–HDTMA	0.17
MMT,SAz-1–BDHDA	0.17	MMT,Swy-2–BDHDA	0.17
MMT,SAz-1–HDP	0.18	MMT,Swy-2–HDP	0.16

Table 2. Maximum absorbed amount of Cu(II) on montmorillonites and their organo-derivatives
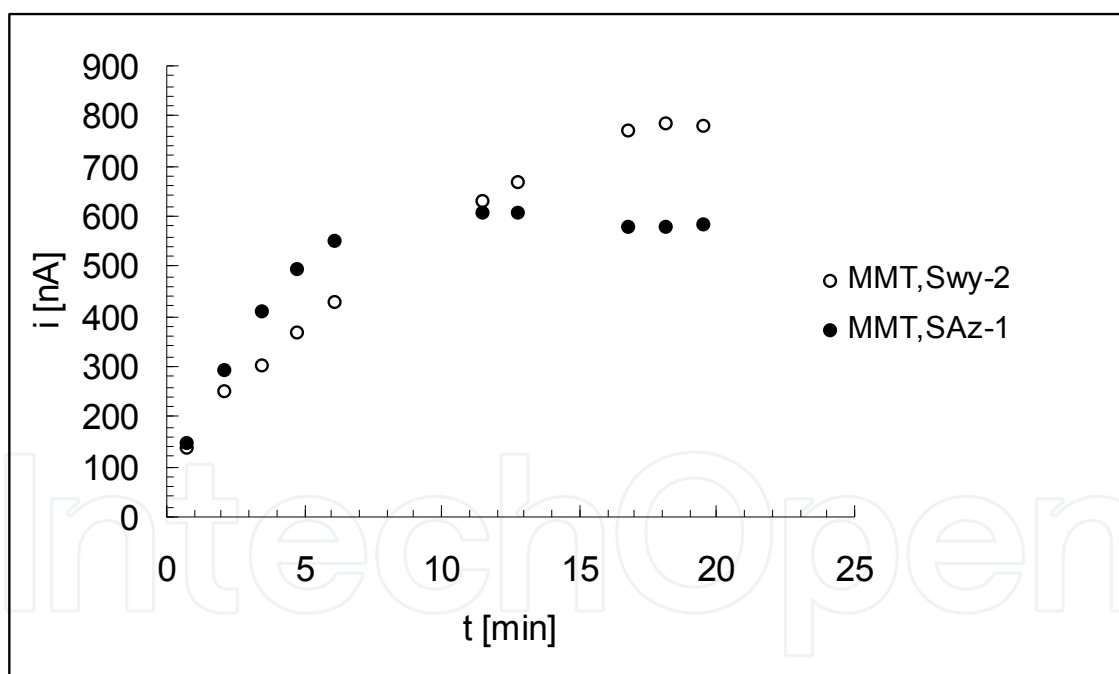
4.3.2. Cyclic voltammetry study

Multisweep cyclic voltammetry (MCV) represents a suitable technique to study adsorption of metals onto a modifier in the carbon paste. In the case of the montmorillonite modifier the obtained current increases with successive occupation of the ion-exchange sites of its structure until a constant, maximum value of current (steady state current) is achieved. The obtained dependences of the current response on a number of cycling (on time) can be used as a characteristic feature for the metals sorption on montmorillonites. The typical multisweep cyclic voltammograms are shown on Figure 8 that depicts MCV of Cu(II) performed on the carbon paste electrode modified with MMT,SAz-1. The successive occupation of the ion-exchange sites of montmorillonite with increasing number of cycling (time) caused the current increase corresponded to the adsorbed amount of Cu(II) [8,10] (the underneath voltammetric peak on Figure 8).

The Cu(II) sorption on two types of montmorillonite – SWy-2 and SAz-1 - was studied by means of multisweep cyclic voltammetry. The obtained current responses on the carbon paste electrodes CPE(MMT,SWy-2) and CPE(MMT,SAz-1) exhibited the time dependences that correspond to the Cu(II) sorption on the montmorillonites (Figure 9). These dependences enable to distinguish the Cu(II) sorption on the various types of montmorillonite. It is seen, that the higher sorption capacity was found in the case of MMT,SWy-2. These finding closely corresponds to the results obtained by the batch technique (Table 2) that proved the slightly higher sorption on the MMT,SWy-2, too.

The multisweep voltammetric study of the Cu(II) sorption on the montmorillonite and its organo-derivative has already demonstrated that the organo-derivative MMT,SAz-1-HDTM exhibited the lower steady state current due to a lower sorption of Cu(II) (Figure 10). The cation exchange sites of the MMT,SAz-1-HDTMA are occupied with the HDTMA cations, which inhibits sorption of the cationic forms Cu^{2+} and $[Cu(ac)]^+$ (ac – acetate) in comparison with the unmodified montmorillonite. HDTM incorporated into the interlayer of MMT,SAz-1 decreased the Cu(II) sorption approximately to   65 % [48].
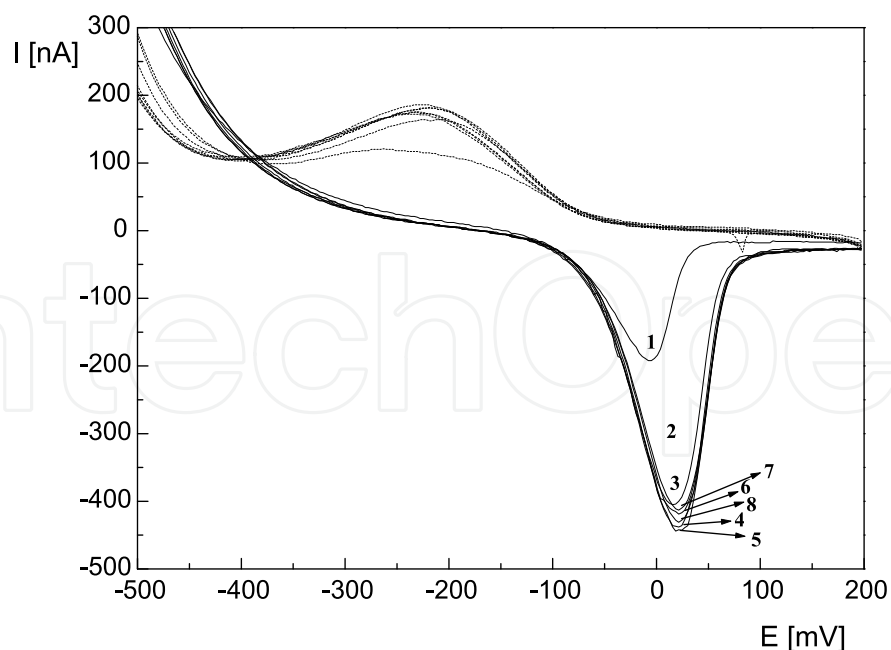
Figure 8. Multisweep cyclic voltammetry of Cu(II) (2.5 x 10^{-5} mol . l^{-1}) in acetate buffer pH 3.6 on CPE(MMT,SAz-1)

Figure 9. Multisweep cyclic voltammetry of Cu(II) (2.5 x 10^{-5} mol .l^{-1}) in acetate buffer pH 3,6 on CPE(MMT,SAz-1) and CPE(MMT,SWy-2)

In this study MCV of the Cu(II) was performed by the same procedure [48] on the carbon paste electrodes modified with the prepared organo-montmorillonites MMT,SAz-1-BDHDA, MMT,SAz-1-HDP, MMT,SWy-2-BDHDA, and MMT,SWy-2-HDP. The MCV voltammograms of Cu(II) performed on the CPEs modified with the organo-montmorillonites in the medium of acetate buffer pH 3.6 – 5.2 were used to construct the

dependence of the maximum current response (steady state current) on the cycling time. The typical dependences in comparison to the above mentioned results [48] are shown on Figure 10. The dependences also indicate the decrease of the steady state current on all organo-montmorillonites in comparison to the original montmorillonite.
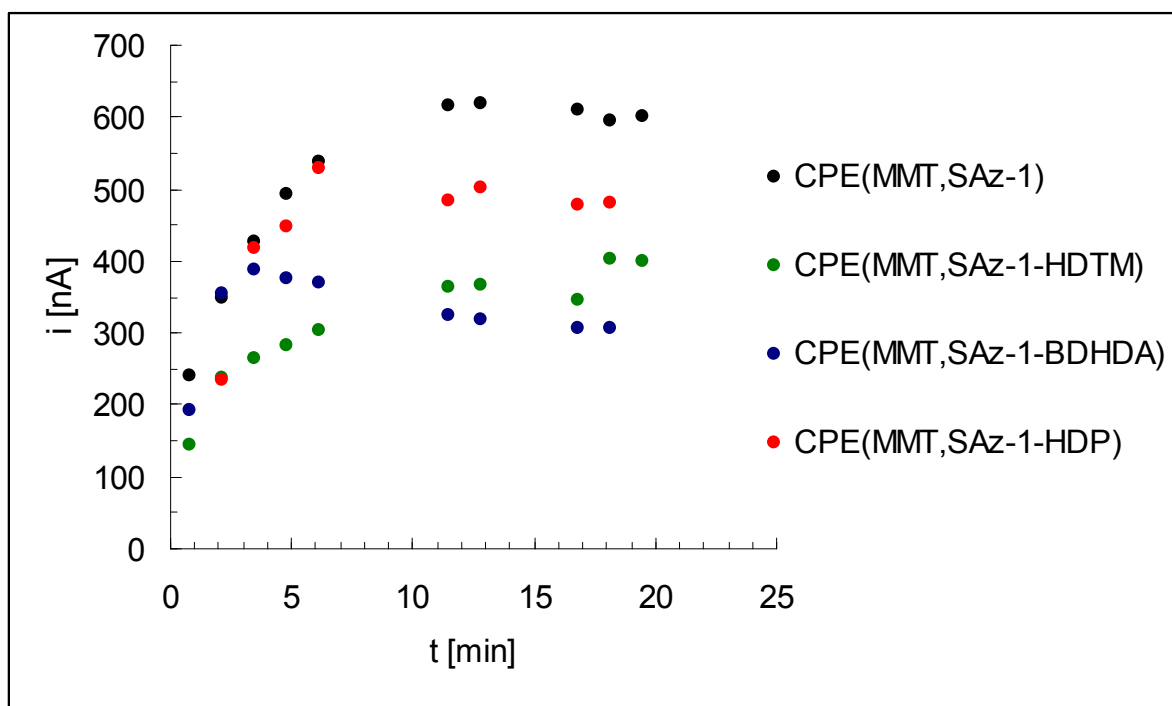
Figure 10. Current vs. t dependences for MCV of Cu(II) (2.5×10^{-5} mol . l^{-1}) in acetate buffer pH 4.0 on CPEs modifed with organo-montmorillonites

The steady state current decrease corresponds to the decrease of the Cu(II) sorption onto the modifier in the carbon paste which is caused by the presence of the alkylammonium cations in the interlayer structure or on the surface of the montmorillonite modifier in the carbon paste electrode. It is seen form Figure 10 that the Cu(II) sorption is decreased on about 80 % and 63 % in the case of MMT,SAz-1-HDP, resp. MMT,SAz-BDHDA.

Although the demonstrated dependences (Figure 9 and 10) cannot be considered as the classical sorption isotherms, they indicates the same characteristics of the Cu(II) sorption:

- the higher sorption capacity to Cu(II) was found for MMT,SWy-2 by means of the classical sorption isotherms as well as by the multisweep cyclic voltammetry on the carbon paste electrodes modified with montmorillonites
- the highest sorption was found on the original montmorillonites by the batch technique as well as by the multisweep cyclic voltammetry on the carbon paste electrode modified with the original montmorillonite
- all prepared organo-montmorillonites exhibited significantly lower sorption capacity for Cu(II) calculated from the adsorption isotherms as well as measured by means of the multisweep cyclic voltammetry on the carbon paste electrode modified with the organo-montmorillonites.

5. Conclusions

The applied electrochemical techniques – measurement of zeta potential and multisweep cyclic voltammetry – offer possibility to study and characterize properties of clay minerals connected with the sorption processes on their surfaces.

The zeta potential measurement is a method suitable for characterization of the clay minerals particles from the point of view of their surface charge that is one of the significant parameters influencing sorption on clay minerals. As it was shown the measurement of zeta potential enable to determine the pH range where the montmorillonite particles did not change significantly the surface charge and where they tend to coagulate. The zeta potential measurement during sorption of Cu(II) exhibited the excellent agreement of the zeta potential dependence on the Cu(II) equilibrium concentration with the adsorption isotherm measured by the classical sorption experiments (batch techniques). Analogously, the same course of the adsorption isotherm and the zeta potential changes in the sorption system of montmorillonite – hexadecyltrimethylammonium cation was found. The zeta potential changes can be compared with its changes on other sorbents (coals). The alkylammonium adsorption way can be evaluated from the zeta potential changes [45].

Multisweep cyclic voltammetry represents another method to characterize the metals sorption using the electrodes modified with a studied adsorbent – clay mineral. The current response dependences on time give the typical curves suitable to describe the sorption. The following general conclusions can be obtained by this method:

- comparison of the individual clay minerals in terms of their sorption capacity
- influence of the alkylammonium presence in the clay mineral on the metals sorption
- influence of other important parameters on the sorption – for example pH, presence of other cations, temperature

The advantage of multisweep cyclic voltammetry consists in relatively fast performance providing the first idea about sorption. For example, measurement on carbon paste electrode takes about 20 – 30 min in comparison with the time-consuming batch sorption experiments – minimum 24 hours. On the other hand, multisweep cyclic voltammetry enable only a semi-quantitative evaluation of sorption.

The described electrochemical methods can be successfully used as the additional methods of study and characterization of clay minerals.

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Acknowledgement

6. References

[1] Ghosh P K, Bard A J (1983) Clay-modified Electrodes. J. am. chem. soc. 105: 5691 - 5693.

[2] Bard A J, Mallouk T (1992) Electrodes Modified with Clays, Zeolites, and Related Microporous Solids. In: Murray R W, editor. Molecular Design of Electrode Surfaces. New York: J. Wiley, New York. pp. 271 - 311.

[3] Fitch A (1990) Clay-modified Electrodes: A Review. Clay. clay miner. 38: 391 - 400.

[4] Macha S M, Fitch A (1998) Clays as aAchitectural Units at Modified Electrodes. Microchim. acta. 128: 1 - 18.

[5] Macha S, Baker S, Fitch A (2002) Clays and Electrochemistry: An Introduction. CMS workshop lectures. 10: 1 - 62.

[6] Villemure G (2002) Electron Transport in Electrodes Modified with Synthetic Clays Containing Electrochemically Active Transition Metal Sites. CMS workshop lectures 10: 149 - 184.

[7] Navratilova Z, Kula P (2003) Clay Modified Electrodes: Present Applications and Prospects. Electroanalysis. 15: 837 - 846.

[8] Fitch A (1990) Apparent Formal Potential Shifts in Ion Exchange Voltammetry. J. electroanal. chem. 284: 237 - 244.

[9] Mousty Ch (2004) Sensors and Biosensors Based on Clay-modified Electrodes – New Trends. Appl. clay sci. 27:159 - 177.

[10] Kula P, Navratilova Z (1994) Voltammetric Study of Clay Minerals Properties. Acta u. carol. geol. 38: 295 - 301.

[11] Kula P, Navratilova Z (1996) Voltammetric Copper(II) Determination with a Montmorillonite-modified Carbon Paste Electrode. Fresenius j. anal. chem. 354: 692 - 695.

[12] Navrátilová Z, Hranicka Z (2008) Montmorillonite Modified Electrodes for Study of Cu Adsorption Kinetics. Sensing in Electroanalysis. 3: 55 – 64.

[13] Kalcher K, Grabec I, Raber G, Cai X, Tavcar G, Ogorevc B (1995) The Vermiculite-modified Carbon Paste Electrode as a Model System for Preconcentrating Mono- and Divalent Cations. J. electroanal. chem. 386: 149 - 156.

[14] Navratilova Z, Kula P (2000) Cation and Anion Exchange on Clay Modified Electrodes. J. solid state electrochem. 4: 342 - 347.

[15] Kula P, Navratilova Z, Kulova P, Kotoucek M (1999) Sorption and Determination of Hg(II) on Clay Modified Carbon Paste Electrodes. Anal. chim. acta. 385: 91 - 101.

[16] Kula P, Navratilova Z (2001) Anion Exchange of Gold Chloro Complexes on Carbon Paste Electrode Modified with Montmorillonite for Determination of Gold in Pharmaceuticals. Electroanalysis. 13: 795 - 798.

[17] Navratilova Z, Kula P (2000) Determination of Gold Using Clay Modified Carbon Paste Electrode. Fresenius j. anal. chem. 367: 369 - 372.

[18] Tonle I K, Ngameni E, Walcarius A (2004) From Clay- to Organoclay-film Modified Electrodes: tuning chargé selectivity in Ion Exchange Voltammetry. Electrochim. Acta. 49: 3435 - 3443.

[19] Grabec-Svegl I, Ogorevc B, Hudnik V (1996) A Methodological Approach to the Application of a Vermiculite Modified Carbon Paste Electrode in Interaction Studies: Influence of Some Pesticides on the Uptake of Cu(II) from a Solutions to the Solid Phase. Fresenius z. anal. chem. 354: 770 - 773.

[20] Kula P, Navratilova Z, Chmielova M, Martinec P, Weiss Z, Klika Z (1996) Modified Electrodes: Sorption of Cu(II) on Montmorillonite - Humic Acid System. Geologica carpathica – series clays 5: 49 - 53.

[21] Tonle I K, Ngameni E, Njopwouo D, Carteret C, Walcarius A (2003) Functionalization of Natural Smectite-type Clays by Grafting with Organosilanes: Physico-chemical Characterization and Application to Mercury(II) Upteke. Phys. chem. chem. phys. 5: 4951 - 4961.

[22] Tonle I K, Ngameni E, Walcarius A (2005) Preconcentration and Voltammetric Analysis of Mercury(II) at a Carbon Paste Electrode Modified with Natural Smectite-type Clays grafted with Organic Chelating Groups. Sensors and actuators B – chemical. 110: 195 - 203.

[23] Ngameni E, Tonle I K, et al. (2006) Permselective and Preconcentration Properties of a Surfactant-intercalated Clay Modified Electrode. Electroanalysis. 18: 2243 - 2250.

[24] Manisankar P, Selvanathan G, Vedhi C (2006) Determination of Pesticides Using Heteropolyacid Montmorillonite Clay-Modified Electrode with Surfactant. Talanta. 68: 686 - 692.

[25] Fernandez L, Borrás C, Carrero H (2006) Electrochemical Behavior of Phenol in Alkaline Media at hydrotalcite-like Clay/Anionic surfactants/Glassy Carbon Modified Electrode. Electrochim. Acta. 52: 872 - 884.

[26] Fernandez M, Fernández L, Borras C, Mostany J, Carrero H (2007) Characterization of Surfactant/Hydrotalcite-like Clay/Glassy Carbon Modified Electrodes: Oxidation of Phenol. Anal. chim. Acta. 597: 245 - 256.

[27] Yang H, Zheng X., Huang W, Wu K (2008) Modification of Montmorillonite with Cationic Surfactant and Application in Electrochemical Determination of 4-chlorophenol. Colloid and surfaces B: biointerfaces. 65: 281 -284.

[28] Newton Dias Filho L, Ribeiro do Carmo D (2006) Study of an Organically Modified Clay: Selectvie Adsorption of Heavy Metal Ions and Voltammetric Determination of Mercury(II). Talanta. 68: 919 - 927.

[29] Marsalek R. (2009) The influence of surfactants on the zeta potential of coals. Energ Source Part. A. 31: 66-75.

[30] Kaluza L, Gulkova D, Vit Z, Zdrazil M. (2007) Tailored Distribution of MoO3 in the TiO2 and ZrO2 Supported Catalysts by Water-Assisted Spreading. Proceedings of European Congress of Chemical Engineering (ECCE-6). Copenhagen, 16-20 September 2007.

[31] Marsalek R. (2011) The Reduction of Zinc using Goethite Process and Adsorption of Pb+II, Cu+II and Cr+III on Selected Precipitate. International journal of environmental science and development (IJESD). Available http://www.ijesd.org/abstract/133-C013.htm. Accessed 2011 APR 8.

[32] Sondi I, Biscan J, Pravdic V (1996) Electrokinetics of Pure Clay Minerals Revisited. Journal of colloids and interface science. 178: 514-522.

[33] Zhuang J, Yu G.R. (2002) Effects of Surface Coating on Electrochemical Properties and Contaminant Sorption of Clay Minerals Chemosphere. 49: 619-628.

[34] Lv L., Tsoi G., Zhao X.S. (2004). Uptake Equilibria and Mechanisms of Heavy Metal Ions on Microporoous Titanosilicate ETS-10.Ind. Eng. chem. res. 43: 7900-7906.

[35] Vittal R, Gomathi H, Kim K J (2006) Beneficial Role of Surfactants in Electrochemistry and in the Modification of Electrodes. Adv. colloid. interface. sci. 119: 55-68.

[36] Wu S F, Yanagisawa K., Nishizawa T (2001) Zeta Potential on Carbons and Carbides. Carbon. 39: 1537-1541.

[37] Navratilova Z, Vaculikova L (2006) Electrodeposition of Mercury Film on Electrodes Modified with Clay Minerals. Chemical Papers. 60: 348–352.

[38] Navratilova Z, Wojtowicz P, Vaculikova L., Sugarkova V (2007). Sorption of Alkylammonium Cations on Montmorillonite. Acta Geodynamica et Geomaterialia. 4: 59–65.

[39] He H, Ma Y, Zhu J, Yuan P, Qing Y (2010) Organoclays Prepared from Montmorillonites with Different Cation Exchange Capacity and Surfactant Configuration. Applied clay science 48: 67 - 72.

[40] Volzone G, Rinaldi J O, Ortiga J (2006) Retention of Gases by Hexadecyltrimethylammonium-montmorillonite Clays. Journal of environmental management 79: 247 - 252.

[41] Betega de Paiva L, Morales A R, Valenzuela Díaz F R (2008) Organoclays: Properties, Preparation and Applications. Applied clay science, 42: 8–24.

[42] Kooli F, Liu Y, Alshahateet S F, Messali M, Bergaya F (2009) Reaction of Acid Activated Montmorillonites with Hexadecyltrimethylammonium Bromide Solution. Applied clay science. 43: 357–363.

[43] Madejova J (2003) FTIR Techniques in Clay Mineral Studies. Vibrational Spectroscopy. 31: 1-10.

[44] Delbem M F et al. (2010) Modification of a Brazilian Smectite Clay with Different Quaternary Ammonium Salts. *Química Nova.* 33: 309-315.

[45] Marsalek R, Navratilova Y (2011) Comparative Study of CTAB Adsorption on Bituminous Coal and Clay Mineral. Chemical Papers. 65: 77 – 84.

[46] Zeng Z, Jiang J (2005) Effects of the Type and Structure of Modified Clays on Adsorption Performance. International journal of environmental studies. 62: 403 – 414.

[47] Gupta S S, Bhattacharyya K G (2006) Adsorption of Ni (II) on Clays. Journal of colloid and interface science. 295: 21 – 32.

[48] Navratilova Z, Hranicka Z (2009) Carbon Paste Electrode Modified with Alkylammonium-clay Composite. Sensing in elecroanalysis 4: 39 – 46.