

MONTMORILLONITE ION EXCHANGED BY MERCURY (II)

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ABSTRACT

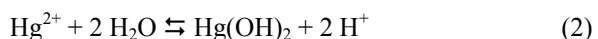
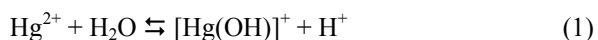
Hg(II) ions dissolved in aqueous solutions were adsorbed by montmorillonite (MMT). The Hg(II) ion-exchange was strongly limited by the competition with H⁺ ions: the maximal amounts of adsorbed Hg(II) and H⁺ ions were 0.21 mmol g⁻¹ and 1.10 mmol g⁻¹, respectively. MMTs saturated with Hg(II) (Hg-MMTs) were examined by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy and thermal analysis. Hg(II) ions, such as Hg²⁺ and [Hg(OH)]⁺, along with H⁺ ones were mostly adsorbed on permanent sites (75 % of cation exchange capacity (CEC)) and also on pH dependent surface sites (25 % of CEC). While heating, Hg-MMTs was losing their mass up to 700 °C as a result of the MMT dehydration and dehydroxylation accompanied by release of adsorbed Hg(II).

KEYWORDS: Hg(II), montmorillonite, ion exchange, hydrogen ions, surface complexes

1. INTRODUCTION

Hg(II) is one of the most important inorganic environmental pollutants. Its main natural source is mineral vermilion (HgS) and other sulphide minerals. Anthropogenic sources are some industrial wastewaters, exhaust gases of fossil fuels, mercury pesticides, and organo-mercury compounds used for conservation and seed dressing. Both organic and inorganic Hg(II) compounds are lipophilic and, therefore, they well accumulate themselves in biomass (Zeroual et al., 2003; Karunasagar et al., 2005). Their toxicity has been known for a long time (Gavis and Ferguson, 1972). Main methods for the Hg(II) removal are based on its adsorption by solid materials (Ali and Gupta, 2006; Monterroso et al., 2011) and precipitation as mercury sulphide.

In order to study the transport of Hg(II) in soil-water systems many studies were carried out to investigate adsorption/desorption mechanisms of Hg(II) by organic and inorganic adsorbents (Liao et al., 2009). Hg(II) ions hydrolyse in aqueous solutions as follows

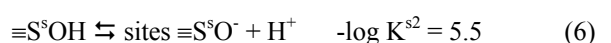


These hydrolytic equilibria are characterized by the hydrolytical constants $\log K_1 = -2.70$ and $\log K_2 = -6.19$ (Sarkar et al., 2000). As obvious, H⁺

ions are released in both reactions and resulting solutions are more acidic than those of other metal cations (Pitter, 2002).

Phyllosilicates having a negative surface charge should be promising ion exchangers for Hg(II) ions. In this context, the Hg(II) ion exchange on several smectites (Guerra et al., 2009), kaolinite (Sarkar et al., 2000), bentonite (Viraraghan and Kapoor, 1994), montmorillonite (Brigatti et al., 2005; Kónya and Nagy, 2011) and vermiculite (Brigatti et al., 2005) was studied.

In general, metals can be adsorbed on permanent and pH dependent surface sites of phyllosilicates (e.g. Bradl, 2004; Churchman et al., 2006). The permanent sites are located in interlayers and the surface sites are represented by hydroxyl groups on external layers and edges. The surface sites are used to be divided into strong (s) and weak (w) ones according to their affinity to metals: the weak sites have a lower affinity for metals and participate in complex forming reactions when the strong sites are already saturated. These sites react with hydrogen ions as follows



where S is Si and Al (e.g. Krapiel et al, 1999; Tournassat et al., 2004), K is the dissociation constant.

The aim of this work was to study the ion exchange of Hg(II) by montmorillonite, which is a predominant clay mineral in bentonites, having the negative layer charge from -0.2 to -0.6 (Bergaya and Lagaly, 2006). Unlike most of authors, who studied the ion exchange of non-specified Hg(II), we took into consideration all pH dependent forms, such as Hg^{2+} , $\text{Hg}(\text{OH})^+$, $\text{Hg}(\text{OH})_2$ and $\text{Hg}(\text{NO}_3)^+$. The effect of hydrogen ions on the Hg(II) ion exchange was observed. The obtained results should be useful for prediction of the Hg(II) movement in soils and for its retention by natural or artificial adsorbents. In addition, the temperature behaviour of exchanged Hg(II) was studied by thermal analysis with respect to possible decontamination of retained Hg(II).

2. EXPERIMENTAL

2.1. MATERIAL AND CHEMICALS

Reagents

The used chemicals were of analytical reagent grade: mercury nitrate, ammonium chloride (all from Lachema, Czech Republic). Water deionised by reverse osmosis (Aqua Osmotic, Czech Republic) was used for the preparation of all solutions.

The < 5 μm fraction of Na^+ -rich montmorillonite (SWy 2) (Crook County, Wyoming) separated by sedimentation was used. Its cation exchange capacity (CEC) of $1.21 \pm 0.06 \text{ meq g}^{-1}$ was calculated from the concentrations of Na^+ , K^+ , Ca^{2+} and Mg^{2+} displaced by repeated saturation with NH_4^+ . The structural MMT formula $\text{Na}_{0.38} \text{K}_{0.04} (\text{Ca}_{0.12} \text{Mg}_{0.50} \text{Fe}^{3+}_{0.41} \text{Al}_{2.90} \text{Ti}_{0.01} \text{Mn}_{0.01}) (\text{Si}_8) \text{O}_{20} (\text{OH})_4$ was calculated from the results of X-ray fluorescence analysis.

Ion exchange procedure

A portion of MMT (cca 0.1 g) was added into 100 ml of $\text{Hg}(\text{NO}_3)_2$ solutions and these dispersions were shaken vigorously for 24 hours. Then, the suspensions were centrifuged for 20 minutes, filtered, and dried gently at 50 °C for 24 hours. Filtrates were analysed by atomic absorption spectrometry (AAS) and alkalimetric titration. The pH in the filtrates changed from 4.4 to 1.9 according to increasing $\text{Hg}(\text{NO}_3)_2$ concentrations (Table 1). The room temperature varied from 20 °C to 24 °C during all experiments. Hg-MMTs were obtained at the initial concentrations of 0.1 mmol l^{-1} to 3.0 mmol l^{-1} ; they were denoted as 0.1Hg-MMT, 0.2Hg-MMT, 0.5Hg-MMT etc.

The ion exchange was studied by means of batch experiments. The exchanged amounts a (mmol g^{-1}) of Hg(II) and H^+ were calculated as follows:

$$a = \frac{(c_0 - c_e)V}{w} \quad (7)$$

where c_0 and c_e are the initial and equilibrium of both Hg(II) and H^+ concentrations (mmol l^{-1}), respectively,

V (l) is the volume of solutions and w (g) is the mass of MMT.

2.2. METHODS

Atomic absorption spectrometry

The concentrations of mercury, sodium, potassium, calcium and magnesium in the filtrates were determined by atomic absorption spectrometer AA280FS (Varian Inc., Australia) with the acetylene-air atomization. Obtained data were processed by the SpectrAA Pro software.

Alkalimetric titration a pH measurements

The concentrations of hydrogen ions were determined by alkalimetric titration of the filtrates with 0.10 mol l^{-1} NaOH. Bromocresol purple was used as an indicator. The pH of the filtrates was measured by a pH-metre WTW InoLab (Weilheim, Germany).

X-ray powder diffraction

The X-ray powder diffraction study was performed by a powder diffractometer (BRUKER D8 ADVANCE) equipped with a scintillation and position-sensitive detector (VANTEC) and a source of CoK_α radiation. The diffraction patterns were recorded in an ambient atmosphere under constant conditions (50 kV, 60 mA). The XRD patterns were identified using the PDF-2-Release 2004 database.

Scanning electron microscopy

An XL 30 Philips SEM instrument (Netherlands) equipped with a Robinson backscattered electron (BSE) and energy dispersive (EDAX) detectors were used for the examination of MMT and Hg-MMTs. The powdered samples were coated with gold and palladium in an ionization chamber before the analysis.

Fourier transform infrared spectrometry

FTIR spectra were obtained by the KBr method using a Nicolet NEXUS 470 Fourier transform spectrometer (ThermoNicolet, USA). The spectrometer was equipped with a Global IR source, KBr beam splitter, and DTGS detector. For each spectrum, 64 scans were obtained with the resolution of 8 cm^{-1} . The recorded FTIR spectra were processed by means of the program OMNIC 7.3. The spectra were normalized for the same mass of MMT.

Thermogravimetry and differential thermal analysis

A thermal analyser Setsys 12 Setaram equipped with a thermal measurement head TG ATD Rod was used. Thermal gravimetry (TG) and differential thermal analysis (DTA) curves were recorded in a static air atmosphere with a heating rate of 10 °C min^{-1} to the final temperature of 1200 °C. The sample mass was about 30 mg.

Data analysis

The experimental data were statistically processed by means of the QC.Expert programme

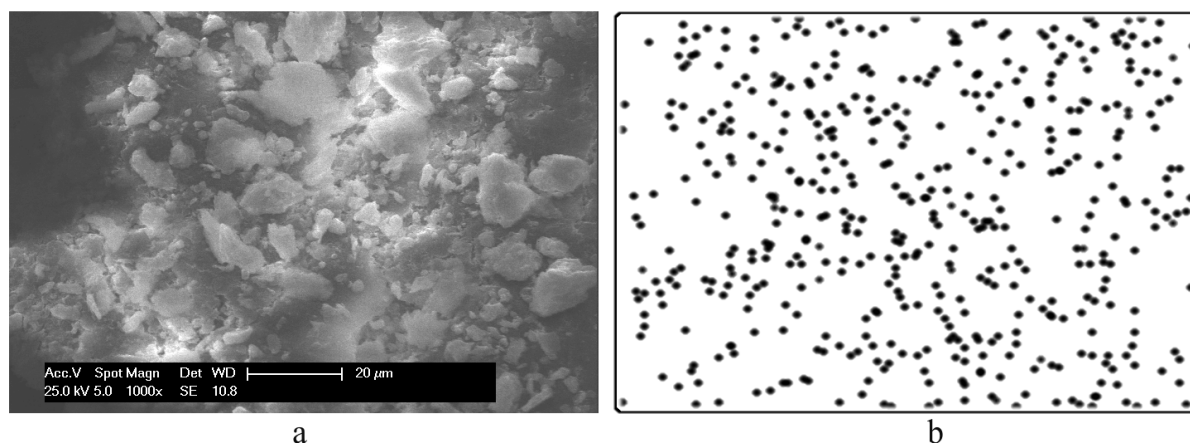


Fig. 1 SEM micrograph and map of 2.0Hg-MMT.

Table 1 Analytical results of the filtrates after the ion exchange.

c_0 of Hg (mmol l ⁻¹)	c_e of Hg (mmol l ⁻¹)	pH	Des. Na ⁺ (meq g ⁻¹)	Des. K ⁺ (meq g ⁻¹)	Des. Ca ²⁺ (meq g ⁻¹)	Des. Mg ²⁺ (meq g ⁻¹)	Des. summa (meq g ⁻¹)
0.10	0.074	4.4	0.417	0.021	0.016	0.028	0.482
0.20	0.103	3.3	0.431	0.025	0.121	0.118	0.696
0.50	0.359	2.7	0.473	0.023	0.195	0.178	0.869
0.80	0.657	2.5	0.466	0.021	0.211	0.200	0.898
1.0	0.852	2.4	0.505	0.023	0.215	0.212	0.955
1.5	1.371	2.2	0.436	0.023	0.236	0.218	0.914
2.0	1.748	2.1	0.431	0.023	0.237	0.218	0.910
3.0	2.909	1.9	0.432	0.023	0.228	0.225	0.908

(TriloByte, Pardubice, Czech Republic). All statistical calculations were performed at the $\alpha = 0.05$ significance level.

3. RESULTS AND DISCUSSION

3.1. X-RAY DIFFRACTION STUDY

The XRD patterns showed that the MMT interlayer spacing d_{001} (2.0Hg-MMT) increased from 11.9 Å to 13.5 Å due to the intercalation of Hg(II) ions. In spite of pH = 2.1 of Hg(II) dispersions, MMT retained its layered structure as confirmed by the presence of narrow and intensive 001 diffraction bands. Since no crystalline Hg(II) form was observed, the adsorption of Hg(OH)₂ was not further considered.

3.2. SCANNING ELECTRON MICROSCOPY STUDY

The used scanning electron microscope was equipped with an energy dispersive detector that enabled the X-ray analysis of various elements. The SEM micrographs were completed by the X-ray spectra and maps of elements distributed on MMT and Hg-MMTs surfaces. The typical SEM micrograph and the Hg(II) map (2.0Hg-MMT) are shown in Figure 1. As obvious, Hg(II) was evenly distributed on the Hg-MMT surface.

3.3. INFRARED SPECTROMETRY STUDY

The FTIR spectra of MMT and Hg-MMTs are shown in Figure 2. The marked absorption bands are specified in Table 2. The stretching OH vibrations of ≡SOH groups in MMT octahedra were observed at 3633 cm⁻¹ ($A(3633)$) and the stretching OH vibrations of adsorbed water were observed at 3420 cm⁻¹. The absorbances at 3420 cm⁻¹ ($A(3420)$) decreased with the Hg(II) loading (Fig. 3) until full MMT saturation was reached. No frequency shifts of the stretching vibrations were observed. The decrease of $A(3420)$ indicates the formation of some complexes at ≡SOH sites.

The absorbances at 3633 cm⁻¹ ($A(3633)$) well correlated with the calculated content X (wt%) of [Hg(OH)]⁺ in the total adsorbed Hg(II). The regression between $A(3633)$ and X was described by the linear equation $A(3633) = 0.0092 X - 0.2818$ ($r = 0.8919$), where X varied from 75 wt% to 65 wt%. In addition, the ratio of [Hg(OH)]⁺/Hg²⁺ changed from 2.9 to 1.9. Figure 3 also indicates that adsorbed [Hg(OH)]⁺ and Hg²⁺ were coordinated by the same number of water molecules n ; very likely $n = 6$ as in Hg(II) aqueous solutions (Greenwood and Earnshaw, 1993). [Hg(H₂O) _{n}]²⁺ has $2n$ OH bonds ($H_2O \propto 2 OH$) and if [Hg(OH)]⁺ would be coordinated with a lower

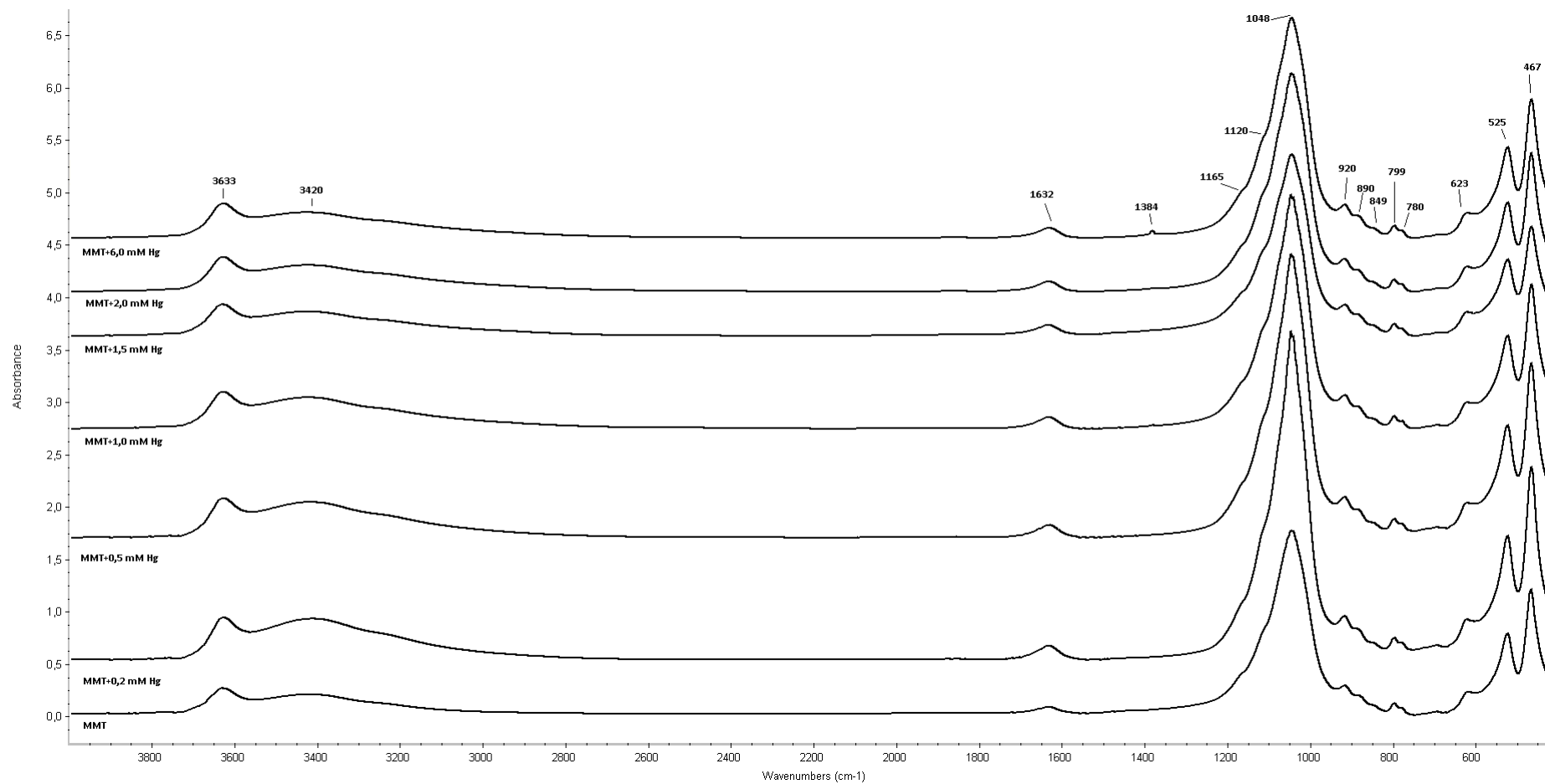
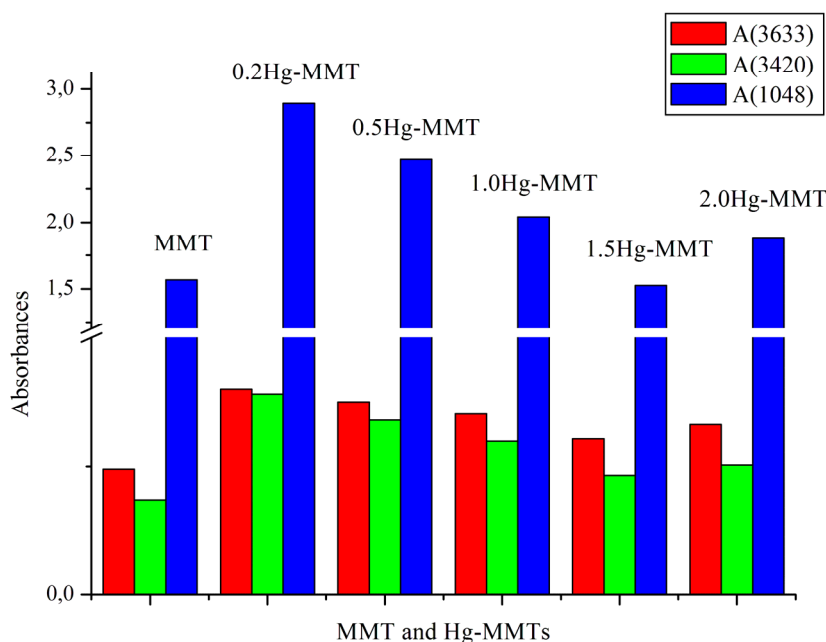


Fig. 2 FTIR spectra of MMT and Hg-MMTs.

Table 2 Interpretation of the FTIR spectra of Hg-MMTs.

Wavenumber (cm ⁻¹)	Vibration modes
3633	stretching vibration of structural O-H
3420	stretching vibration of O-H in water (moisture)
1632	bending vibration of O-H in water (moisture)
1384	stretching vibration of nitrate
1165 (shoulder)	stretching vibration of Si-O (silica)
1120 (shoulder)	axial mode of stretching vibration of Si-O
1048	stretching vibration of Si-O
920	bending vibration of Al-Al-OH
890 (shoulder)	bending vibration of Al-Fe-OH
849 (shoulder)	bending vibration of Al-Mg-OH
799	stretching vibration of Si-O (silica)
780	stretching vibration of Si-O (silica)
623	coupled out of plane bending vibrations of Al-O a Si-O
525	bending vibration of Al-O-Si
467	bending vibration of Si-O-Si

**Fig. 3** Plots of absorbances at 3633 cm⁻¹, 3420 cm⁻¹ and 1048 cm⁻¹ of MMT and Hg-MMTs.

number of waters, e.g. $n-1$, then $[\text{HgOH}(\text{H}_2\text{O})_{n-1}]^+$ would have $2n-1$ OH bonds and, consequently, the $A(3633)$ plot should be increasing.

In addition, the absorbance at 1048 cm⁻¹ ($A(1048)$) corresponding to SiO stretching vibrations also decreased with the loading of Hg(II) as shown in Figure 3. It can be explained by the change of the SiO dipole moment μ . For its intensity I it holds: $I \approx (\partial\mu/\partial l)^2$, where l is the distance between Si and O (Nakamoto, 1986). Mercury has higher electronegativity than the interlayer cations but lower one than oxygen which led to shifts of binding electrons

from Si to O. This negative inductive effect was mediated by OH bonds in $\text{Hg}(\text{OH})^+$ and interlayer water. As a result, $A(1048)$ of 0.2Hg-MMT steeply increased. With the higher Hg(II) loading hydrogen ions were bound to oxygen atoms and their partial negative charge decreased. As a consequence, the SiO dipole moment was probably reduced.

In addition, a small band of residual nitrate at 1384 cm⁻¹ was observed only in case of 6.0Hg-MMT. No $\text{Hg}(\text{NO}_3)^+$ referred by other authors (e.g. Sarkar et al., 2000) and nitrate were identified in the FTIR spectra of other Hg-MMTs. Therefore, the ion

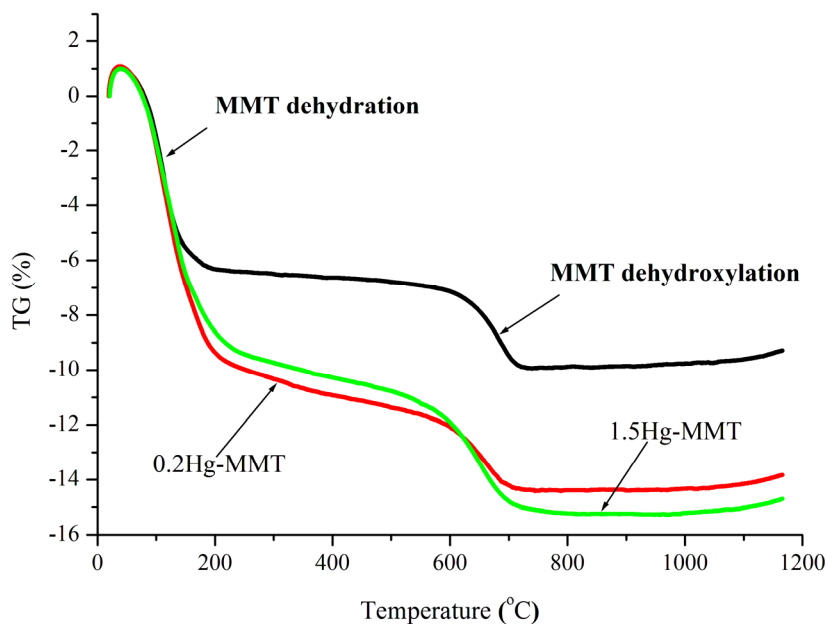


Fig. 4 TG and DTA records of MMT and Hg-MMTs.

exchange of Hg^{2+} and $[\text{Hg}(\text{OH})]^+$ was only taken into account in following calculations.

3.4. THERMAL ANALYSIS STUDY

MMT and Hg-MMTs were also examined by TG and DTA (Fig. 4). In general, the TG records of montmorillonites show reduction of their mass in two steps: i) dehydration of interlayer cations and ii) dehydroxylation of the MMT structure (Fajnor and Jesenák, 1996). Hg-MMTs lost more mass at the dehydration step (10 wt% to 11 wt%) than MMT (6.5 wt%). Water hydrating the interlayer and also Hg(II) ions were released (Brigatti et al., 2005). During the dehydroxylation, Hg-MMTs lost more mass (14-15 wt%) than MMT (10 wt%). It can be explained by the release of MMT hydroxyl groups and Hg(II) ions forming inner-sphere and/or outer-sphere complexes at MMT surface sites. At about 700 °C, the mass of MMT and Hg-MMTs became constant.

3.5. ION EXCHANGE STUDY

The ion exchange isotherms are shown in Figure 5. The maximal adsorbed amount of H^+ (1.10 mmol g^{-1}) was 5-folds higher than that of Hg(II) (0.21 mmol g^{-1}). The sum of the desorbed interlayer cations (Table 1) reached 0.91 meq g^{-1} , i.e. 75 % of CEC (1.21 meq g^{-1}). The amounts (in milliequivalents) of exchanged Hg^{2+} and $[\text{Hg}(\text{OH})]^+$ were calculated from those of exchanged Hg(II) and H^+ using the hydrolytical constant K_1 (8) and the mass balance (9) as

$$K_1 \approx \frac{c_r(\text{H}^+)c_r([\text{Hg}(\text{OH})]^+)}{c_r(\text{Hg}^{2+})} = \frac{a(\text{H}^+)a([\text{Hg}(\text{OH})]^+)}{a(\text{Hg}^{2+})} \quad (8)$$

$$a(\text{Hg}(\text{II})) = a(\text{Hg}^{2+}) + a([\text{Hg}(\text{OH})]^+) \quad (9)$$

where c_r and a are the relative equilibrium concentrations and adsorbed amounts of H^+ and Hg(II) ions, respectively. The maximal exchanged amounts of Hg(II) and H^+ ions were calculated at 0.27 meq g^{-1} and 0.94 meq g^{-1} , respectively. Their sum of 1.21 meq g^{-1} is very close to CEC, which implicates that 75 % (see above) of Hg(II) and H^+ was exchanged on the permanent sites and 25 % on the surface sites. Under the experimental conditions, pH changed from 4.4 to 1.9 and, therefore, Hg(II) inner-sphere and outer-sphere complexes on $\equiv\text{S}^{\text{w}}\text{OH}$ and $\equiv\text{S}^{\text{s}}\text{OH}$ sites are expected to be formed (see Eqs. 3-6). Similarly, the surface sites were protonated forming $\equiv\text{S}^{\text{w}}\text{OH}_2^+$, $\equiv\text{S}^{\text{s}}\text{OH}_2^+$ and $\equiv\text{S}^{\text{s}}\text{OH}$. Figure 5 also shows that the exchanged amounts of Hg(II) gradually decreased (triangles) at the higher equilibrium concentrations because of the competitive ion exchange of H^+ ions.

CONCLUSION

In this study, the ion exchange of Hg(II) by MMT was studied. The exchanged amounts were strongly limited by the competition with H^+ ions. Hg(II) ions were mostly adsorbed on MMT permanent sites (intercalated) and also formed complexes on surface sites. The thermal analysis of Hg-MMTs

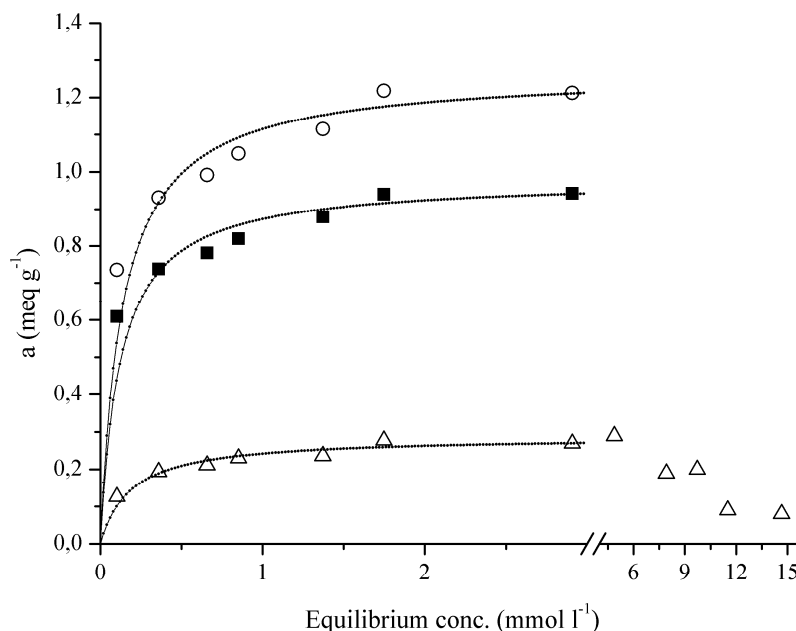


Fig. 5 Ion exchange isotherms of Hg(II) and H⁺ ions. Hg(II) (Δ), H⁺ (\blacksquare), sum of Hg(II) and H⁺ (\circ).

showed the two-step mass decrease up to 700 °C during which water and Hg(II) released.

The obtained results should be useful in cases when Hg(II) will be ion exchanged by clays, which will be further decontaminated: e.g. for prediction of Hg(II) movement in soils, treatment of wastewaters, building protection barriers and so forth. In next research, Hg(II) complex-forming reactions on various phyllosilicates will be studied in details.

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