Modified aluminosilicates as low-cost sorbents of As(III) from anoxic groundwater

Barbora Doušová [a,*], Lucie Fuitová [a], Tomáš Grygar [b], Vladimír Machovič [a,c], David Koloušek [a], Lenka Herzogová [a], Miloslav Lhotka [a]

[a] Institute of Chemical Technology in Prague, Technická 5, 166 28 Prague 6, Czech Republic
[b] Institute of Inorganic Chemistry AS CR, 250 68 Řež, Czech Republic
[c] Institute of Rock Structure and Mechanics ASCR, V Holešovičkách 41, 182 09 Prague 8, Czech Republic

ABSTRACT

The utilization of low-grade clay materials as selective sorbents represents one of the most effective possibilities of As removal from contaminated water reservoirs. The simple pre-treatment of these materials with Fe (Al, Mn) salts can significantly improve their sorption affinity to As oxyanions. The natural kaolin calcined at 550 °C (mostly metakaolin) and raw bentonite (mostly montmorillonite) pre-treated with Fe^{II}, Fe^{III}, Al^{III} and Mn^{II} salts were used to remove of As from the model anoxic groundwater with As^{III} concentration about 0.5 and 10 mg L^{-1}. All the pre-treating methods were appropriate for bentonite; the efficiency of As^{III} sorption varied from 92 to >99%, by the sorption capacity higher than 4.5 mg g^{-1}. In the case of metakaolin, Fe^{II}- and Mn^{II}-treatments proved the high sorption efficiency (>97%), while only <50% of As was removed after Fe^{III} and Al^{III} pre-treatment. The sorption capacities of treated metakaolin ranged from 0.1 to 2.0 mg g^{-1}.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

People from many regions of India, Bangladesh and Latin American countries suffer (even nowaday) from serious diseases with symptoms typical to arsenic poisoning. A natural geologic origin of As was proved in many studies [1–4], but the mechanism of its release into the groundwater has not been clarified up to now. The weathering of As-rich pyrite and arsenopyrite occured in discrete layers [5,6] and/or the release of arsenic from As–FeOOH surface complexes under reduction conditions [4,7,8] are considered the most probable reasons of strong As enrichment in aquifers. The untreated groundwater is then used as a sole source of drinking and/or irrigation water in poor rural and urban areas of the above mentioned countries [1,3,9,10].

Various technologies have been developed for the arsenic removal from aqueous systems. Adsorption methods fall into the most commonly used procedures due to a variability of natural and synthetic sorbents [11–14]. Most of conventional and non-conventional treating methods were compared in the critical

review by Mohan and Pittman Jr. [15]. Iron oxides and oxyhydroxides are the most widespread and effective sorbents for inorganic As forms both in natural environments (soils, bottom sediments, etc.) and in technological processes [16–19]. However, their synthesized forms are too expensive and hardly available for wide use. Additionally, only a tiny surface fraction of Fe ions is really active in the sorption on bulk oxides, hence supporting of the iron oxides on finely dispersed, cheap, well-processable and environmentally friendly matrix is very desirable.

Recently aluminosilicates have opened new posibilities in sorption technology due to favourable surface properties, availability, environmental and economical reasons. In general, they are not selective sorbents of anionic contaminants thanks to a low value of the pH_{ZPC}. Therefore, more and more studies have been focused on the preparation of anion-selective sorbents by the surface pre-treatment of aluminosilicates such as clays and sands [12,20–22]. Besides the sorption efficiency, a mechanism of surface processes has gained more importance in precise characterization of newly prepared sorbents [23–25].

The main aim of this work was to verify two different types of raw clays (bentonite and calcined kaolin) pre-treated with Fe^{II}, Fe^{III}, Al^{III} and Mn^{II} particles as selective sorbents of As^{III} from model anoxic groundwater strongly contaminated with As.

* Corresponding author. Tel.: +420 220443798.
E-mail address: Barbora.Dousova@vscht.cz (B. Doušová).

Table 1
XRF analysis and specific surface area S_{BET} of raw materials.

Sorbent	SiO$_2$ (% wt)	Al$_2$O$_3$ (% wt)	Fe$_2$O$_3$ (% wt)	MnO (% wt)	S_{BET} (m^2/g)
MT	58.00	37.20	2.06	0.01	8.65
BT	51.50	20.60	14.60	0.11	73.10

2. Materials and methods

2.1. Raw clays

Two different types of clays, kaolin and bentonite used in this work represented second rate materials easily available at a commercial scale. Expected prices (less than 30 EUR per 1 tonne) have been only connected with handling and transporting costs. Kaolin sample contained kaolinite and lesser amounts of quartz and micas. Its quality was much decreased by the large content of Fe (Table 1). After the thermal treatment (calcination at 500 °C for 3 h to metakaolin) Fe species in kaolin were transformed to a red oxide (α-Fe$_2$O$_3$, hematite) that by no means interfered with As sorption. Calcined kaolin has been marked further as MT.

Bentonite sample (BT) contained mostly montmorillonite with traces of quartz. It was mined in a pit on an industrial scale and ground only in an agate mortar before use. The relative content of main elements obtained by XRF is summarized in Table 1 together with the specific surface areas of both samples.

2.2. Treating procedures

During the interaction of raw clay and a metal salt solution, reactive ion-exchangeable species and very poorly crystalline hydrated oxide particles in stable oxidation state (Fe^{III}, Al^{III}, Mn$^{III/IV}$) have been formed on the solid surface.

The pre-treatment with Fe^{II} salt consisted of the agitation of raw sorbent (20 g) with 0.6 M FeSO$_4$·7H$_2$O (1 L) in a sealed polyethylene bottle at ambient temperature for 24 h. Then the solid phase was filtered off, washed with distilled water, dried at 60 °C, and homogenized [26].

In the treatment with Fe^{III} salt 20 g of raw sorbent was mixed with 10 mL of 2 M Fe(NO$_3$)$_3$. The suspension was dried at 110 ± 10 °C for 24 h. Then the product was filtered off, washed with distilled water, dried at 60 °C, and homogenized [27].

To Al^{III} pre-treatment 4 M NaOH was dropped into 10 mL of 1 M AlCl$_3$·6H$_2$O up to pH about 6.0, until AlOOH has been formed; well-agitated suspension of AlOOH with 20 g of raw sorbent was dried at 70 °C for 1 day. Then the product was filtered off, washed with distilled water, dried at 60 °C, and homogenized [28].

The procedure with Mn^{II} salt was developed by Herzogová [29]. The suspension of 0.8 M MnSO$_4$·H$_2$O (1 L) alkalized with 1 M NaOH to pH about 8.0–8.2, and 20 g of raw sorbent was agitated in sealed polyethylene bottle at laboratory temperature for 24 h. Then the solid phase was filtered off, washed with distilled water, dried at 60 °C, and homogenized.

The relative growth of metal fractions in pre-treated clays is demonstrated in Fig. 1.

2.3. Model solutions

According to Stüben et al. [2], Tandukar et al. [3], Bhattacharya et al. [8], and Nickson et al. [30], the composition of model solutions was inferred from an average composition of real anoxic groundwater with a different content of arsenic. MOD I and MOD II solutions were prepared from FeSO$_4$·7H$_2$O, MnSO$_4$·H$_2$O, NaHCO$_3$ and NaAsO$_2$ of p.a. quality and distilled water under N$_2$ atmosphere, to actual composition: 6.0 mg L^{-1} of Fe^{2+}; 0.8 mg L^{-1} of Mn^{2+}; 500.0 mg L^{-1} of HCO$_3$$^-$; 130.0 mg L^{-1} of SO$_4$$^{2-}$; 0.5 mg L^{-1} (MOD I) and 10 mg L^{-1} (MOD II) of AsO$_3$$^{3-}$, respectively.

2.4. As sorption

The suspension of model solution (50 mL) with the defined amount of pre-treated sorbent (0.3–2.5 g L^{-1} for MOD I and 3.0–18.0 for MOD II) was shaken in sealed polyethylene bottle at laboratory temperature (20 °C) for 72 h, according to Doušová et al. [23]. The product was filtered off; the filtrate was analyzed for residual As
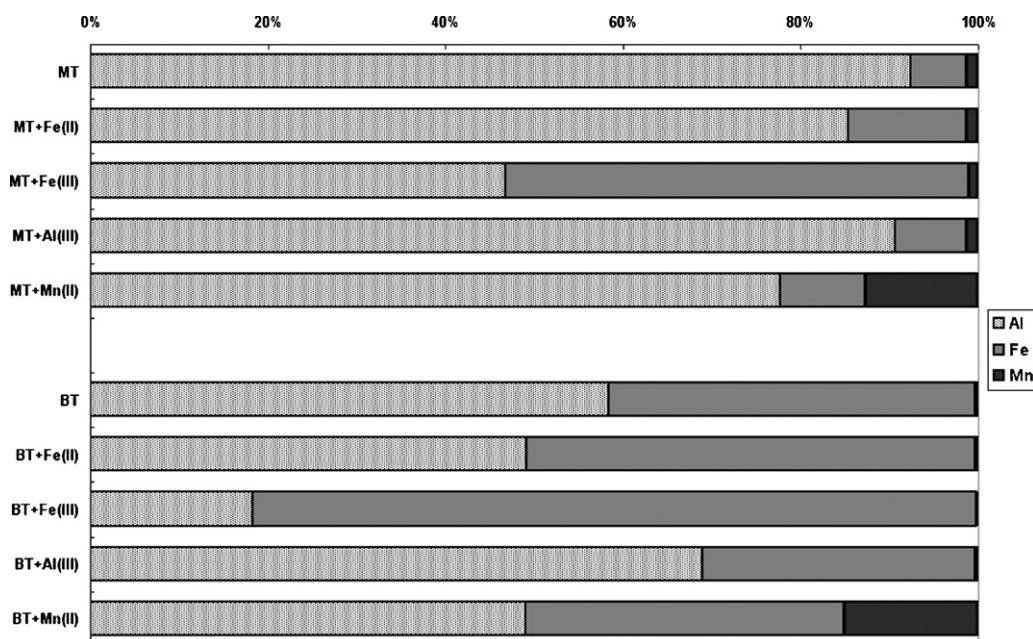

Fig. 1. Relative growth of metal fractions of Fe, Al and Mn in pre-treated sorbents; MT—metakaolin, BT—bentonite.

content, while the solid part was tested with the methods mentioned below (IR spectroscopy, diffuse reflectance spectroscopy, and voltammetry of microparticles).

2.5. Leaching tests

The stability of As in saturated sorbents was verified by usual procedure EN 12457-2 [31]; the suspension of dry sorbent and distilled H_2O in the ratio of 1:10 was agitated in sealed polyethylene reactor at laboratory temperature for 6 h and then aged under the same conditions for 18 h. The product was filtered off and the filtrate was analyzed for As content.

2.6. Analytical methods

Powder X-ray diffraction samples were measured using a Seifert XRD 3000P diffractometer with Co K_α radiation ($\lambda = 0.179026$ nm, graphite monochromator, goniometer with Bragg–Brentano geometry) in 2θ range 5–60° step size 0.05° 2θ.

XRF analyses of solid phase were determined by ARL 9400 XP+ spectrometer; voltage 20–60 kV, probe current 40–80 mA; effective area 490.6 mm². For data evaluation the UniQuant software was used.

Table 2
Sorption capacities and sorption efficiency of modified sorbents.

Sorbent	Q (mg g^{-1})		ε (%)	
	MOD I	MOD II	MOD I	MOD II
MT–Fe^{II}	2.0	1.4	96.5	98.8
MT–Fe^{III}	1.6	3.8	47.0	77.2
MT–Al^{III}	1.8	0.8	98.7	47.8
MT–Mn^{II}	1.7	1.3	97.7	92.2
BT–Fe^{II}	4.5	4.3	99.8	99.9
BT–Fe^{III}	3.3	7.3	99.8	99.7
BT–Al^{III}	4.1	1.3	86.3	86.8
BT–Mn^{II}	4.7	3.0	98.3	98.8

The concentration of As in aqueous solutions was determined by AAS using SpectrAA-880, unit VGA 77 (Varian) for measuring in flame and SpectrAA-300 (Varian) for hydride process.

The IR spectra were measured on a Nicolet 740 Fourier transform infrared spectrometer equipped with a TGS detector. The KBr pellet technique was used at the resolution of 2 cm^{-1} and 32 accumulations of the spectrum.

Voltammetry of microparticles was performed with a conventional paraffin impregnated graphite electrode in a 1:1 acetate buffer with total acetate concentration 0.2 M in linear sweep mode from open circuit potential in the negative direction a scan rate of 3 mV/s [32]. The potentials are given with respect to a saturated
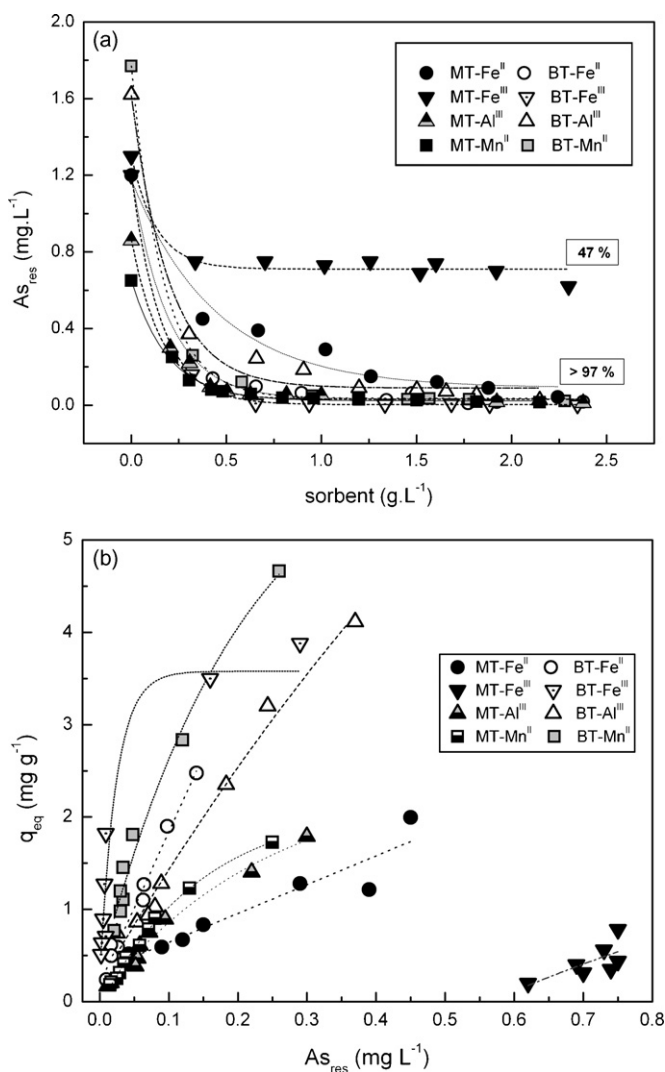

Fig. 2. MOD I sorption series: (a) sorption efficiency and (b) sorption capacity.
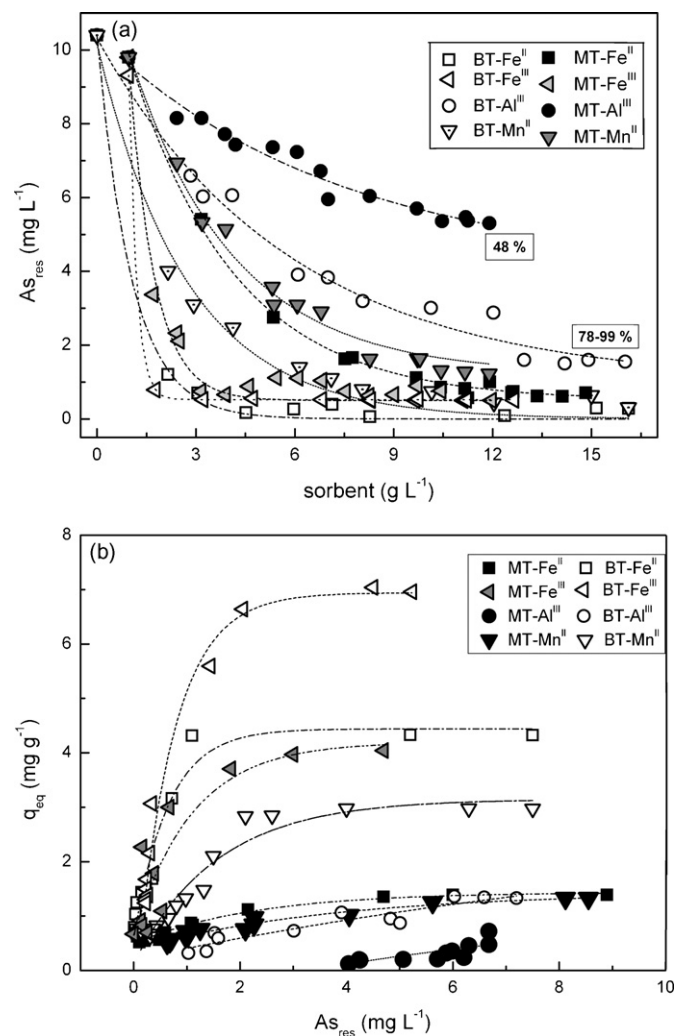

Fig. 3. MOD II sorption series: (a) sorption efficiency and (b) sorption capacity.

calomel reference electrode (SCE) and interpreted by comparing with the peak potentials E_p of reference oxides [32], and free Fe^{3+} ions and oligomeric Fe^{III} hydroxo-oxide species [24].

2.7. Quality control of applied methods

An accuracy of AAS analyses has been guaranteed by the Laboratory of atomic absorption spectrometry, ICT Prague (CR); the detection limit = 0.5 μg L^{-1} by the standard deviation $\approx$5–10%. The reproducibility of pre-treated methods and leaching tests was checked by parallel experiments; the standard deviation resulted from 10 experimental sets ranged from 4.5 to 12.6% for the pre-treatment procedures, while it did not exceed 5% for the leaching tests.

3. Results and discussion

3.1. Efficiency of sorption processes

The sorption capacity q_{eq} (mg g^{-1}) represents the equilibrium amount of As adsorbed on the sorbent surface, while the sorption efficiency (%) is calculated from the residual As concentration (As$_{res}$) in the solution [33].

The selectivity of modified sorbents for MOD I is demonstrated in Fig. 2 and Table 2. Except Fe^{III} pre-treated MT, all prepared sorbents proved available for As removal; the sorption efficiency exceeded 97% at equilibrium sorption capacities about 2.0 mg g^{-1} for MT, and 3.0–7.0 mg g^{-1} for BT. The results were similar for extremely contaminated groundwater simulated as MOD II (Fig. 3 and Table 2), where the MT–Al^{III} pre-treatment was least effective (<50%). The worse sorption efficiency of MT–Fe^{III} and MT–Al^{III} systems could be related to the steric effect of hydrolyzed particles of Fe^{III} (Al^{III}) in the treating solution. The FeOOH (AlOOH) aggregates formed in the treating solutions were probably too large for bonding to active surface sites of metakaolin and spread over its surface. The different shapes of sorption isotherms for both the investigated models (compare Fig. 2a and 3b) resulted from a different As content in MOD I and MOD II; as expected, through the sorption of As from low-concentrated solution (MOD I), the active surface sites have never been fully saturated and adsorption isotherms tended to increase continuously, on the other hand, the sorption isotherms of more As concentrated water (MOD II) showed the saturated equilibrium area, characterized with constant values of sorption capacities. A higher sorption capacity of modified BT related partly to its larger specific surface area (Table 1) and its different surface properties, but mostly to the different metal oxide species formed in the both aluminosilicate carriers. The reached adsorption capacities corresponded well with Li et al. [21] and Elizade-Gonzáles et al. [33]; in both cases the actual sorption capacity significantly depended on initial As concentration.

3.2. Mechanism of surface processes

As already mentioned, the surface pre-treatment of clays resulted in new sorbents enriched in hydrated metal particles in reactive, ion-exchangeable surface positions [34].
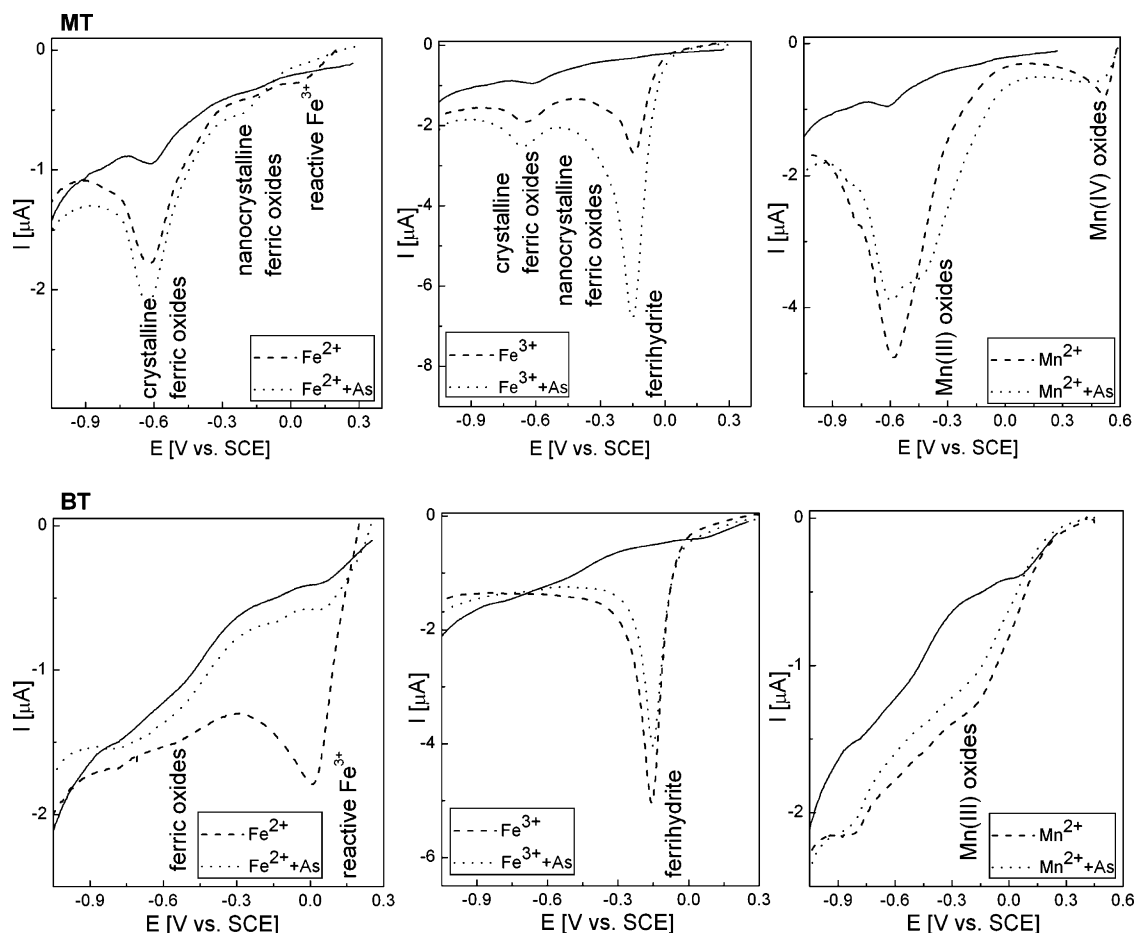

Fig. 4. Voltametric curves of Fe^{II}, Fe^{III} and Mn^{II} pre-treated sorbents before- and after-As sorption; MT—metakaolin, BT—bentonite.
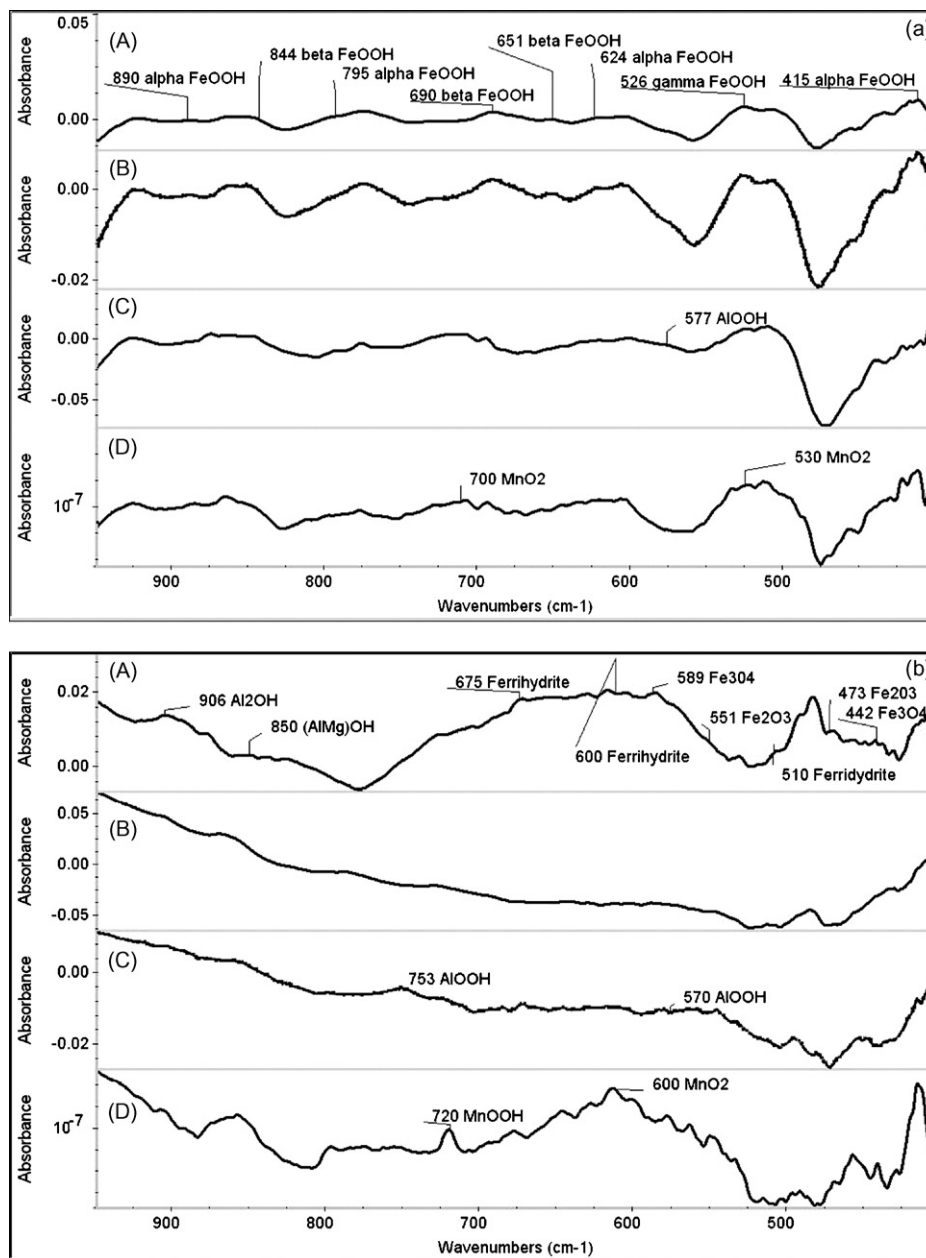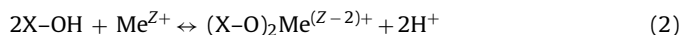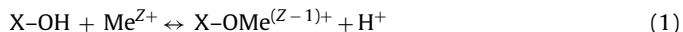
Fig. 5. IR spectra of pre-treated sorbents for identification of arised metal phases: (a) MT and (b) BT; subtracted spectra for Fe^{III} (A), Fe^{II} (B), Al^{III} (C), Mn^{II} (D) pre-treatment.

$$X–OH + Me^{Z+} \leftrightarrow X–OMe^{(Z-1)+} + H^+ \qquad (1)$$

$$2X–OH + Me^{Z+} \leftrightarrow (X–O)_2Me^{(Z-2)+} + 2H^+ \qquad (2)$$

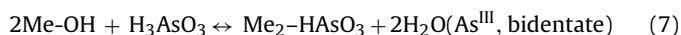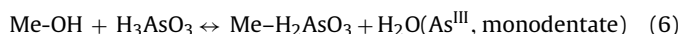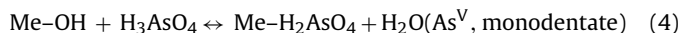$$X–OH + Me^{Z+} + H_2O \leftrightarrow X–OMeOH^{(Z-2)} + 2H^+ \qquad (3)$$

where $X \approx$ Si, Al; Me $\approx$ Fe, Al, Mn.

Voltametric curves in Fig. 4 and infrared spectra in Fig. 5 proved the substantial variability in the metal oxide phases depending on the aluminosilicate carrier and the treating process. In the case of Fe^{II} treatment, the originally present Fe$_2$O$_3$ particles grew further in MT, while in the reactive interlayer of BT, Fe^{III} species were formed. These species were characteristic to Fe^{III}-treated montmorillonite, too [24]. After Mn^{II} pre-treatment, different metal oxide species were formed on the solid surface of two carriers: Mn$^{III/IV}$ oxides on MT and Mn^{III} oxides on BT. The Fe^{III} treatment of both carriers produced ferrihydrite: much better sorption properties of

Fe^{III}-treated BT related probably to the larger specific surface S_{BET} of raw bentonite. As was already mentioned, the treatment with Al^{III} proceeded in a similar manner as with Fe^{III}; hydrolyzed metal particles in a treating solution have been coagulated to AlOOH aggregates (see Fig. 5a and b). The detailed study of Fe/Mn phase transformations depending on surface properties and aging time was found in [35–38].

During As adsorption most of the active sites were stabilized in Me–As surface complexes according to following formulas [35,37]:

$$Me–OH + H_3AsO_4 \leftrightarrow Me–H_2AsO_4 + H_2O (As^V, \text{monodentate}) \quad (4)$$

$$2Me–OH + H_3AsO_4 \leftrightarrow Me_2–HAsO_4 + 2H_2O (As^V, \text{bidentate}) \quad (5)$$

$$Me–OH + H_3AsO_3 \leftrightarrow Me–H_2AsO_3 + H_2O (As^{III}, \text{monodentate}) \quad (6)$$

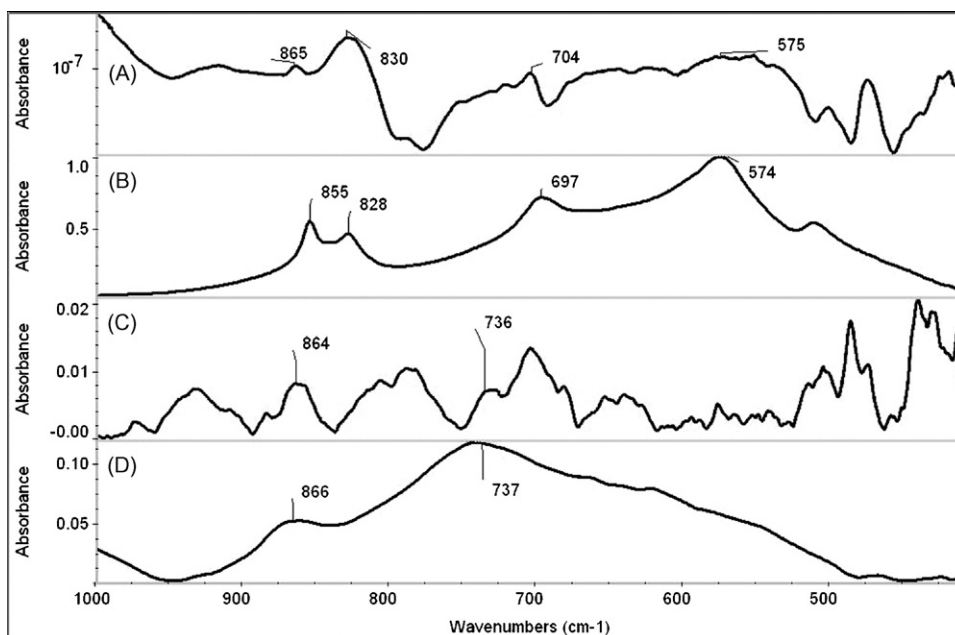$$2Me-OH + H_3AsO_3 \leftrightarrow Me_2–HAsO_3 + 2H_2O (As^{III}, \text{bidentate}) \quad (7)$$

Fig. 6. IR spectra of As-saturated sorbents; A—subtraction of Mn[II] pre-treated MT with As[III] adsorbed/Mn[II] pre-treated MT, B—As[III] standard, C—subtraction of Al[III] pre-treated BT with As[III] adsorbed/Al[III] pre-treated BT, D—As[V] standard.

Adsorption affinity of As species depending on surface properties were also described in [17].

Unoccupied sites have been transformed to more stable and/or crystalline mineral phases of appropriate metal (goethite, boehmite, manganite) during the sorption process [25,38].

IR spectra of As-saturated sorbents (Fig. 6) verified, that As[III] could be bound both as As[III] and As[V] to sorbent surface; in case of MT, AsO_3^{3-} ions did not change the initial valence during the sorption process and were observed in the trivalent state (spectra A, B). The As–O bands at about 860, 830, 700 and 575 cm^{-1} assigned to As[III] form (compare A and B spectra). The sorption on BT indicated two possibilities: while Fe[II]/Mn[II]-treated BT behaved as treated MT, after Fe[III] as well as Al[III] treatment of BT, only the bands at 738 and 870 cm^{-1} derived from AsO_4^{3-} were found (spectra C, D), which confirmed the oxidation of AsO_3^{3-} to AsO_4^{3-} during the sorption process. Oxidation accompanying sorption of AsO_3^{3-} on Fe[III] modified montmorillonite was also reported by Izumi et al. [39]. The final oxidation state of adsorbed AsO_3^{3-} has probably been connected with the character of accumulated metal particles on the sorbent surface (small single Fe[III], Mn[III/IV] particles contrary to FeOOH, AlOOH aggregates), sorption kinetics and at last, possible oxidizing environment on the surface of solid phase.

3.3. Stability of As in saturated sorbents

Stability of spent sorbents has only rarely been addressed in previous studies but it seems vital to be checked with respect to the metastability of poorly crystalline hydrous metal oxides. The results of leaching test are summarized in Table 3. As released into water solution varied from <0.1 to >4.0% wt, depending on the binding character of As–Me surface complexes and the surface charge of solid phase. According to EPA and WHO guidelines [40,41], all measured As values in leaches were under the admissible limit. The long-term stability of spent sorbents under conditions similar to waste deposits should be tested in the near future.

Table 3
Stability of As in saturated sorbents.

Sorbent	As in solid phase (mg g^{-1})	As leached (%)
MT–Fe[II]	0.7	1.3
MT–Fe[III]	1.8	0.1
MT–Al[III]	0.4	4.4
MT–Mn[II]	0.8	1.5
BT–Fe[II]	1.6	0.8
BT–Fe[III]	0.1	0.8
BT–Al[III]	0.8	0.8
BT–Mn[II]	1.4	3.4

4. Conclusions

The described methods opened new possibilities of effective and cheap decontamination of As polluted aqueous systems. It has been applicable to almost all aluminosilicates, even to low-grade or waste sources, which represent low-cost and widely available material with favourable surface properties. Aluminosilicates are not the selective sorbents of anionic contaminants, however, their simple pre-treatment with Fe, Al and Mn salts enabled to prepare anion-selective sorbents with high sorption efficiency (>95%). The experiments with two different types of clays (metakaolin and raw bentonite) proved, that all pre-treating methods were successful with bentonite; in the case of metakaolin, Fe[II]- and Mn[II]-treatments were much more effective (sorption efficiency > 97%), than Fe[III] and Al[III] pre-treatment, when less than 50% of As was removed from the initial solution. As[III] could be bound both in trivalent and pentavalent states to sorbent surface depending on the structure of raw material (steric properties, surface charge), treating method and/or the quality of initial solution (pH, As[III] concentration, competitive ions).

References

[1] S.K. Acharyya, B.A. Shah, Genesis of arsenic contamination of groundwater in alluvial Gangetic aquifer in India, in: J. Bundschuh, P. Bhattacharya, D. Chandrasekharam (Eds.), Natural Arsenic in Groundwater: Occurrence, Remediation and Management, Balkema, London, 2005, pp. 17–23.

[2] D. Stüben, Z. Berner, D. Chandrasekharam, J. Karmakar, Arsenic enrichment in groundwater of West Bengal, India: geochemical mobilization of As under reducing conditions, Appl. Geochem. 18 (2003) 1417–1434.

[3] N. Tandukar, P. Bhattacharya, G. Jacks, A.A. Valero, Naturally occuring arsenic in groundwater of Terai region in Nepal and mitigation options, in: J. Bundschuh, P. Bhattacharya, D. Chandrasekharam (Eds.), Natural Arsenic in Groundwater: Occurrence, Remediation and Management, Balkema, London, 2005, pp. 41–48.

[4] Y. Zheng, M. Stute, A. van Geen, I. Gavrieli, R. Dhar, H.J. Simpson, P. Schlosser, K.M. Ahmed, Redox control of arsenic mobilization in Bangladesh groundwater, Appl. Geochem. 19 (2004) 201–214.

[5] A. Chatterjee, D. Das, B.K. Mandal, T.R. Chowdhury, G. Samanta, D. Chakraborti, Arsenic in groundwater in six districts of West Bengal, India: the biggest arsenic calamity in the world. Part I. Arsenic species in drinking water and urine of the affected people, Analyst 120 (1995) 643–650.

[6] K.G. Stollenwerk, G.N. Breit, A.H. Welch, J.C. Yount, J.W. Whitney, A.L. Foster, M.N. Uddin, R.K. Majumder, N. Ahmed, Arsenic attenuation by oxidized aquifer sediments in Bangladesh, Sci. Total Environ. 379 (2–3) (2007) 133–150.

[7] K.M. Ahmed, P. Bhattacharya, M.A. Hasan, S.H. Akhter, S.M.M. Alam, M.A.H. Bhuyian, M.B. Imam, A.A. Khan, O. Sracek, Arsenic enrichment in groundwater of the alluvial aquifers in Bangladesh: an overview, Appl. Geochem. 19 (2004) 181–200.

[8] P. Bhattacharya, J. Jana, B. Nath, S.J. Sahu, D. Chatterjee, G. Jacks, Groundwater As mobilization in the Bengal Delta Plain, the use of ferralite as a possible remedial measure—a case study, Appl. Geochem. 18 (2003) 1435–1451.

[9] J.M. Cole, M.C. Ryan, S. Smith, D. Bethune, Arsenic source and fate at a village drinking water supply in Mexico and its relationship to sewage contamination, in: J. Bundschuh, P. Bhattacharya, D. Chandrasekharam (Eds.), Natural Arsenic in Groundwater: Occurrence, Remediation and Management, Balkema, London, 2005, pp. 67–75.

[10] F. Wagner, Z.A. Berner, D. Stüben, Arsenic in groundwater in the Bengal Delta Plain: geochemical evidences for small scale redox zonation in the aquifer, in: J. Bundschuh, P. Bhattacharya, D. Chandrasekharam (Eds.), Natural Arsenic in Groundwater: Occurrence, Remediation and Management, Balkema, London, 2005, pp. 3–15.

[11] D. Mohan, C.U. Pittman Jr., M. Bricka, F. Smith, B. Yancey, J. Mohammad, P.H. Steele, M.F. Alexandre-Franco, V. Gómez-Serano, H. Gong, Sorption of arsenic, cadmium and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production, J. Colloid Interface Sci. 310 (2007) 57–73.

[12] A. Ramesh, H. Hasegawa, T. Maki, K. Ueda, Adsorption of inorganic and organic arsenic from aqueous solutions by polymeric Al/Fe modified montmorillonite, Sep. Purif. Technol. 56 (2007) 90–100.

[13] C.H. Niu, B. Volesky, D. Cleiman, Biosorption of arsenic (V) with acid-washed crab shells, Water Res. 41 (2007) 2473–2478.

[14] M. Urík, S. Čerňanský, J. Švec, A. Šimonovičová, P. Littera, Biovolatilization of arsenic by different fungal strains, Water Air Soil Pollut. 186 (2007) 337–342.

[15] D. Mohan, C.U. Pittman Jr., Arsenic removal from water/wastewater using adsorbents—a critical review, J. Hazard. Mater. 142 (2007) 1–53.

[16] J. Antelo, M. Avena, S. Fiol, R. López, F. Arce, Effects of pH and ionic strength on the adsorption of phosphate and arsenate at the goethite-water interface, J. Colloid Interface Sci. 285 (2005) 476–486.

[17] Z. Lin, R.W. Puls, Potential indicators for the assessment of arsenic natural attenuation in the subsurface, Adv. Environ. Res. 7 (2003) 825–834.

[18] D.M. Sherman, S.R. Randall, Surface complexation of arsenic(V) to iron(III) (hydr)oxides: structural mechanism from ab initio molecular geometries and EXAFS spectroscopy, Geochim. Cosmochim. Acta 67 (22) (2003) 4223–4230.

[19] B. Doušová, D. Koloušek, F. Kovanda, V. Machovič, M. Novotná, Removal of As(V) species from extremely contaminated mining water, Appl. Clay Sci. 28 (1–4) (2005) 31–43.

[20] V.K. Gupta, V.K. Saini, N. Jain, Adsorption of As(III) from aqueous solution by iron oxide-coated sand, J. Colloid Interface Sci. 288 (2005) 55–60.

[21] Z. Li, R. Beachner, Z. Mc Manama, H. Hanlie, Sorption of arsenic by surfactant-modified zeolite and kaolinite, Micropor. Mesopor. Mater. 105 (2007) 291–297.

[22] Y. Xu, T. Nakajima, A. Ohki, Adsorption and removal of arsenic(V) from drinking water by aluminum-loaded Shirasu zeolite, J. Hazard. Mater. B92 (2002) 275–287.

[23] B. Doušová, T. Grygar, A. Martaus, L. Fuitová, D. Koloušek, V. Machovič, Sorption of As^V on aluminosilicates treated with Fe^{II} nanoparticles, J. Colloid Interface Sci. 302 (2006) 424–431.

[24] T. Grygar, D. Hradil, P. Bezdička, B. Doušová, L. Čapek, O. Schneeweiss, Fe(III) modified montmorillonite and bentonite: Synthesis, chemical and UV–vis spectral characterization, arsenic sorption, and catalysis of oxidative dehydrogenation of propane, Clays Clay Miner. 55 (2) (2007) 165–176.

[25] D. Masih, I. Izumi, K. Aika, Y. Seida, Optimization of an Iron intercalated montmorillonite preparation for the removal of arsenic at low concentrations, Eng. Life Sci. 7 (1) (2007) 52–60.

[26] D. Bonin, Method of removing arsenic species from an aqueous medium using modified zeolite minerals, US Patent 6,042,731 (2000).

[27] M. Edwards, M.M. Benjamin, Adsorptive filtration using coated sand: a new approach for treatment of metal-bearing wastes, J. WPCF 61 (9) (1989) 1523–1533.

[28] W.H. Kuan, S.L. Lo, M.K. Wang, Ch.F. Lin, Removal of Se(IV) and Se(VI) from water by aluminium-oxide-coated sand, Water Res. 32 (3) (1998) 915–923.

[29] L. Herzogová, Adsorption of Se oxyanions on modified clays, Diploma Thesis, ICT Prague, Czech Republic, 2007, p. 87 (in Czech).

[30] R.T. Nickson, J.M. Mc Arthur, P. Ravenscroft, W.G. Burgess, K.M. Ahmed, Mechanism of arsenic release to groundwater, Bangladesh and West Bengal, Appl. Geochem. 15 (2000) 403–413.

[31] CEN, Characterization of waste-Leaching-Compliance test for leaching of granular waste material and sludge. Part 2. One stage batch test at a liquid to solid ratio of 10 L/kg with article below 4 mm, EN 12457-2, Comite Europeen de Normalisation, Brusells, 2002.

[32] T. Grygar, P. Bezdička, D. Hradil, A. Doménech-Carbó, F. Marken, L. Pikna, G. Ceprià, Voltametric analysis of iron oxide pigments, Analyst 127 (2002) 1100.

[33] M.P. Elizade-González, J. Mattusch, W.D. Einicke, R. Wennrich, Sorption on natural solids for arsenic removal, Chem. Eng. J. 81 (2001) 187–195.

[34] M. Ramstedt, Chemical processes at the water-manganite (γ-MnOOH) interface, Ph.D. Thesis, Umea University, Sweden, 2004, p. 74.

[35] R.T. Wilkin, R.W. Puls, Carbon and sulphur accumulation and iron mineral transformation in permeable reactive barriers containing zero-valent iron, in: 2001 Int. Containment & Remediation Technol. Conf. and Exhibition, June 10–13, Orlando, FL, 2001 (CD-ROM).

[36] B.A. Manning, S.E. Fendorf, B. Bostick, D.L. Suarez, Arsenic(III) oxidation and arsenic (V) adsorption reactions on synthetic birnessite, Environ. Sci. Technol. 36 (2002) 976–981.

[37] B.A. Manning, S.E. Fendorf, S. Goldberg, Surface structures and stability of arsenic(III) on goethite: spectroscopic evidence for inner-sphere complexes, Environ. Sci. Technol. 32 (1998) 2383–2388.

[38] D.J. Burleson, R.L. Penn, Two-step growth of goethite from ferrihydrite, Langmuir 22 (2006) 402–409.

[39] Y. Izumi, D. Masih, K. Aika, Y. Seida, Characterization of intercalated iron(iii) nanoparticles and oxidative adsorption of Arsenite on them monitored by X-ray absorption fine structure combined with fluorescence spectrometry, J. Phys. Chem. B 109 (2005) 3227–3232.

[40] EPA, Re-establishes lower arsenic limit for drinking water, Water News for December 16, 2005, US EPA, 2006.

[41] WHO, Official Journal of the European Communities, No. L 23, 26 (2004), pp. 3–16.