

## MODIFIED LOW-GRADE ALUMINOSILICATES AS EFFECTIVE SORBENTS OF HAZARDEOUS OXYANIONS FROM AQUEOUS SYSTEMS

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### ABSTRACT

Arsenic, antimony and selenium belong to toxic contaminants with high environmental risk. In contrast to metal cationic contaminants (Be, Zn, Cd, Hg Pb, etc.) the metalloids and nonmetals of groups 5 and 6 of periodic system generally form the oxyanions in two oxidizing states (i.e. arsenates and arsenites, antimonates and antimonites, as well as selenates and selenites) in dependence on redox potential and pH value. It is well known that above mentioned oxyanions have a strong adsorption affinity to hydrated oxides and/or oxides hydroxides of Fe, Al and Mn, preferably Fe forming stable surface complexes. In fact, commercially produced Fe oxides-based sorbents are too expensive for strongly contaminated aqueous systems. Aluminosilicates have opened new possibilities in sorption technology due to favourable surface properties, availability, environmental and economical reasons, but they are not selective sorbents of anionic contaminants thanks to a low  $pH_{ZPC}$ . A simple Fe/Al/Mn pre-treatment of raw aluminosilicates can significantly improve their sorption affinity to oxyanionic contaminants, including arsenites and arsenates, selenites and selenates and antimonites and antimonates, respectively. Different types of natural and/or second-rate clays (metakaolines with the large content of Fe, raw bentonites and natural clinoptilolite-rich tuff, ) from Central European localities were used for Fe<sup>II</sup>, Fe<sup>III</sup>, Al<sup>III</sup> and Mn<sup>II</sup> pre-treatment.

**KEYWORDS:** toxic oxyanions, adsorption, Fe/Al/Mn modification, aluminosilicates

### 1. INTRODUCTION

Arsenic, selenium and recently also antimony have been of an increasing environmental attention due to their risk to human health. Arsenic and antimony are highly toxic; they are carcinogenic, mutagenic and teratogenic (Plant et al., 2005; Filella et al., 2002). In contrast to arsenic and antimony, trace concentrations of selenium are essential for human and animal health. Despite the necessity for selenium, the range of intake between selenium deficiency (<40  $\mu\text{g}\cdot\text{d}^{-1}$ ) and selenium toxicity (selenosis) (>400  $\mu\text{g}\cdot\text{d}^{-1}$ ) is very narrow in humans (WHO, 1996). The physical and chemical properties of all considered elements intermediate between metals and nonmetals, whereas arsenic is usually described as a metalloid and selenium as a nonmetal. Antimony demonstrates the most metallic features. The geochemistry and environmental behaviour of arsenic, antimony and selenium are very similar because of the same inorganic species abounded. In contrast to metal cationic contaminants (Be, Zn, Cd, Hg Pb, etc.) the metalloids and nonmetals of groups 5 and 6 of periodic system generally form the oxyanions in two oxidizing states (i.e. arsenates and arsenites, antimonates and antimonites, as well as selenates and selenites) in dependence on redox potential and pH value.

Except naturally occurring arsenic in strongly contaminated groundwater from many regions of India, Bangladesh and Latin American countries, where the hazardous concentrations of As have appeared as a result of the strong water-rock interactions and the physical and geochemical conditions for As mobilization in aquifers (Acharyya and Shah, 2005; Stüben et al., 2003; Stollenwerk et al., 2007; Bromssen et al., 2008), the significant part of environmental As/Se/Sb risk comes from anthropogenic sources concerning arsenic-based insecticides and pesticides, fertilizers and wastes from mine, smelter, tannery and glass industries, electronics, photochemistry, coal combustion. Antimony can be considered quite modern but significant forward-looking contaminant due to its increasing use as a flame retarding additive (Filella et al., 2002).

One of the most effective and commonly used method among the decontamination technologies is the adsorption of toxic compounds from aqueous system on both natural and synthetic sorbents (Altundogan et al., 2002; Halter and Pfeifer, 2001; Doušová et al., 2003). In natural systems As/Se/Sb oxyanions have a strong adsorption affinity to hydrated oxides and/or oxides hydroxides of Fe, Al and Mn, preferably Fe, forming stable surface

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

Sorbent	SiO <sub>2</sub> (% wt)	Al <sub>2</sub> O <sub>3</sub> (% wt)	Fe <sub>2</sub> O <sub>3</sub> (% wt)	MnO (% wt)	TiO <sub>2</sub> (% wt)	$S_{\text{BET}}$ (m <sup>2</sup> /g)
K1	58.02	37.22	2.06	0.01	0.24	8.7
K2	57.84	38.73	0.50	-	1.09	7.5
BT	51.50	20.60	14.55	0.11	5.25	73.1
CL	73.90	14.79	1.58	0.03	0.18	24.3
MO	65.55	22.34	1.79	0.109	0.27	61.5

complexes (Randall et al., 2001; Lin and Puls, 2003; Plant et al., 2005; Filella et al., 2002). Iron oxides and oxyhydroxides rank among common substances in the environment, therefore if present, they should create effective accumulator of inorganic As/Se/Sb compounds both in natural environment (soils, bottom sediments, etc.) and in technological processes (Antelo et al., 2005; Sherman and Randall, 2003; Doušová et al., 2005). These sorbents are commercially produced, however, they are too expensive for application to strongly and/or continuously contaminated systems.

During the last ten years aluminosilicates have been checked out in many technologies including adsorption processes due to their favourable surface properties, availability, environmental and economical reasons. Unfortunately, they are not suitable sorbents for anionic contaminants thanks to a low value of  $\text{pH}_{\text{ZPC}}$ . A simple pre-treatment of raw aluminosilicate with metal (Fe, Al, Mn) ions can significantly improve their sorption affinity to oxyanionic contaminants, including arsenites and arsenates, selenites and selenates and antimonites and antimonates, respectively (Gupta et al., 2005; Izumi et al., 2005; Doušová et al., 2006). An initial material behaves like the carrier of hydrated metal oxides layer, which creates anionic-active adsorption sites on the solid surface. Additionally, only a tiny surface fraction of metal ions is really active in the sorption on bulk oxides, therefore, supporting of the metal oxides on finely dispersed, cheap, and environmentally friendly matrix has become very desirable (Gupta et al., 2005; Li et al., 2007; Xu et al., 2002).

The main objectives of this work were to describe four different pre-treating methods (with Fe<sup>II</sup>, Fe<sup>III</sup>, Al<sup>III</sup> and Mn<sup>II</sup> particles) and to compare their application to several types of low-cost, even waste aluminosilicates (metakaolines, bentonites and natural clinoptilolite-rich tuff) from Central European region.

## 2. MATERIALS AND METHODS

### 2.1. RAW ALUMINOSILICATES

Four types of aluminosilicates characterized by different structural, chemical and surface properties were investigated in this work:

**K1** – kaolin from Kadaň, West Bohemia, Czech

Republic 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 hours to metakaolin) Fe species in kaolin were transformed to a red oxide ( $\alpha\text{-Fe}_2\text{O}_3$ , hematite) that by no means interfered with anionic adsorption.

**K2** – lower-grade kaolin from Horní Bříza, West Bohemia, Czech Republic, calcined at 550 °C for 6 hours, consisted of kaolinite (55 % wt.), quartz (30 % wt.) and micas (15 % wt.).

**BT** – raw bentonite from Kadaň, West Bohemia, Czech Republic 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.

**CL** – natural clinoptilolite-rich tuff from the Nižný Hrabovec deposit, Slovak Republic contained mostly clinoptilolite (60 – 80 %), and less amount of muscovite and cristobalite.

**MO** – mineralogically pure, standard Ca-rich montmorillonite SAz-2 (Arizona, USA) was used as comparative sample.

The relative contents of main elements in raw sorbents obtained by XRF were summarized in Table 1, together with the specific surface  $S_{\text{BET}}$  of investigated materials.

### 2.2. PRE-TREATING PROCESS, QUALITY CONTROL

The crucial change of adsorption properties (especially of the  $\text{pH}_{\text{ZPC}}$  value) consisted in the formation of tiny metal ions fraction on the solid surface. During the interaction of raw clay and a metal salt solution running in batch manner, reactive ion-exchangeable and very poorly crystalline particles in stable oxidation state (Fe<sup>III</sup>, Al<sup>III</sup>, Mn<sup>III/IV</sup>) have been arisen on the solid surface.

**Fe<sup>II</sup>** – 20 g of raw sorbent with 1 l of 0.6 M FeSO<sub>4</sub>·7H<sub>2</sub>O prepared under N<sub>2</sub> atmosphere were agitated in a sealed polyethylene bottle at ambient temperature for 24 hours. Then the solid phase was filtered off, washed with distilled water, dried at 50 °C, and homogenized (Bonin, 2000).

**Fe<sup>III</sup>** – 20 g of raw sorbent with 1 l of 0.025 M Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and 0.05 M NaOH (partly hydrolyzed) were agitated in a sealed polyethylene

bottle at ambient temperature overnight. Then the solid phase was filtered off, washed with distilled water, dried at 50 °C, and homogenized (Edwards and Benjamin, 1989).

**Al<sup>III</sup>** - 4M NaOH was dropped into 250 ml of 1M AlCl<sub>3</sub>·6H<sub>2</sub>O up to pH about 6.0, until AlOOH precipitation has been formed; the suspension of prepared AlOOH with 20 g of raw sorbent was agitated in a sealed polyethylene bottle at ambient temperature for 24 hours. Then the solid phase was filtered off, washed with distilled water, dried at 40 °C, and homogenized (Kuan et al., 1998).

**Mn<sup>II</sup>** - the suspension of 0.8M MnSO<sub>4</sub>·H<sub>2</sub>O (1 l) alkalinized with 1M 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 hours. Then the solid phase was filtered off, washed with distilled water, dried at 40 °C, and homogenized (Herzogová, 2007).

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.

### 2.3. MODEL SOLUTIONS

As<sup>III</sup>/As<sup>V</sup> and Se<sup>IV</sup>/Se<sup>VI</sup> solutions in the concentration about 5×10<sup>-4</sup> mol.l<sup>-1</sup> for K2, MO and 2×10<sup>-3</sup> mol.l<sup>-1</sup> for K1, BT, CL were prepared from NaAsO<sub>2</sub>/KH<sub>2</sub>AsO<sub>4</sub> and Na<sub>2</sub>SeO<sub>3</sub>·5H<sub>2</sub>O/Na<sub>2</sub>SeO<sub>4</sub> of analytical-grade quality and distilled water, at ambient temperature (25 °C).

### 2.4. As/Se ADSORPTION

The suspension of model solution (50 ml) with defined amount of sorbent (2-12 g.l<sup>-1</sup>) was shaken in sealed polyethylene bottles at laboratory temperature (20 °C) for 24-96 hours. The product was filtered off; the filtrate was analyzed for residual As/Se content, while the solid part was tested with the methods mentioned below.

### 2.5. ANALYTICAL METHODS

Powder X-ray diffraction samples were measured using a Seifert XRD 3000P diffractometer with CoK<sub>α</sub> radiation (λ= 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 mm<sup>2</sup>. For data evaluation the UniQuant software was used.

BET surface area was measured with Micromeritics' ASAP 2020 (Accelerated Surface Area and Porosimetry) analyzer using the gas sorption technique to generate high-quality data. Available options include the micropore estimation, a high-vacuum option, and a chemisorption option. ASAP 2020 Models include single- and multipoint BET

surface area, Langmuir surface area, Temkin and Freundlich isotherm analyses, pore volume and pore area distributions in the mesopore and macropore ranges by the BJH method using a variety of thickness equations including a user-defined, standard isotherms, pore volume and total pore volume in a user-defined pore size range, micropore distribution by the MP method and total micropore volume by the t-plot and α plot methods, F-ratio plots that illustrate the difference between theoretical and experimental isotherm data, heat of adsorption. The micropore option using Horvath-Kavazoe method, N<sub>2</sub> as analysis adsorptive and analysis bath temperature at -195.8 °C were used for this work.

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<sup>-1</sup> and 32 accumulations of the spectrum.

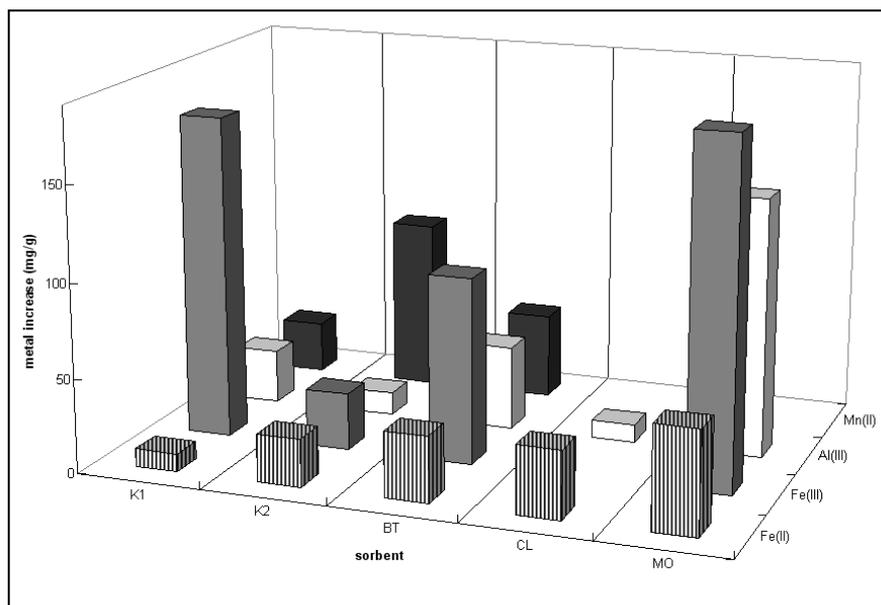
Voltammetry of microparticles was performed with a conventional paraffin impregnated graphite electrode in a 1:1 acetate buffer with total acetate concentration 0.2 M in linear sweep mode from open circuit potential in the negative direction a scan rate of 3 mV/s (Grygar et al., 2002). The potentials are given with respect to a saturated calomel reference electrode (SCE) and interpreted by comparing with the peak potentials E<sub>p</sub> of reference oxides (Grygar et al., 2002), and free Fe<sup>3+</sup> ions and oligomeric Fe<sup>III</sup> hydroxo-oxide species (Grygar et al., 2007).

The residual concentrations of Fe/Al/Mn after treating process and/or As/Se after adsorption in aqueous solutions were determined by AAS using SpectrAA-880, unit VGA 77 (Varian) for measuring in flame and SpectrAA-300 (Varian) for hydride process.

## 3. RESULTS AND DISCUSSION

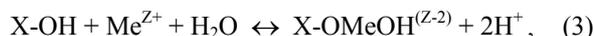
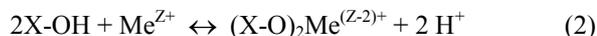
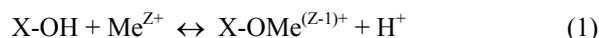
### 3.1. THE MECHANISM AND INTENSITY OF TREATING PROCESS

In natural aqueous systems (pH ~ 5.5–6.5) anionic contaminants including As/Se/Sb oxyanions proved a strong adsorption affinity for hydrated Fe (Al, Mn) oxides and/or oxyhydroxides, which behaved as anion exchangers in mildly acidic and neutral environment thanks to the high value of pH<sub>ZPC</sub> (~ 8.0). These phases predominantly formed very stable inner-sphere surface complexes (Bruce et al., 1998; Sherman and Randall, 2003; Doušová et al., 2005), but weaker outer-sphere complexes, even ion-exchangeable bonds could also participate in equilibrium solid-liquid system. On the other hand, aluminosilicates are not selective sorbents for anionic contaminants thanks to the low value of pH<sub>ZPC</sub> (~ 2.0–4.5). However, the simple modification of their surface could significantly change the surface properties (Doušová et al., 2006). A raw material then served as the carrier of hydrated metal oxides layer, which created active anion exchangeable adsorption sites on the solid surface. This procedure resulted in



**Fig. 1** Relative growth of metal fractions of Fe, Al and Mn in pre-treated sorbents.

new sorbents enriched in hydrated Fe (Al, Mn) particles in reactive, ion-exchangeable surface positions (Ramstedt, 2004).



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

The relative growth of metal fractions in modified sorbents is demonstrated in Figure 1.

The obtained results demonstrate a different intensity of pre-treated process, which related to the composition and mineralogical structure of raw clay, whereas the specific surface value seemed to be dominant (compare with Table 1). The pure montmorillonite (MO), which were used as a reference material, proved the highest affinity to metal ions in all applied procedures, while less than half metal arise was achieved with the metakaolines (K1, K2) pre-treatment. Importantly, a lower metal increase was not succeeded by an ineffective adsorption.

### 3.2. THE VARIABILITY OF METAL PHASES ARISING ON CLAY SURFACE

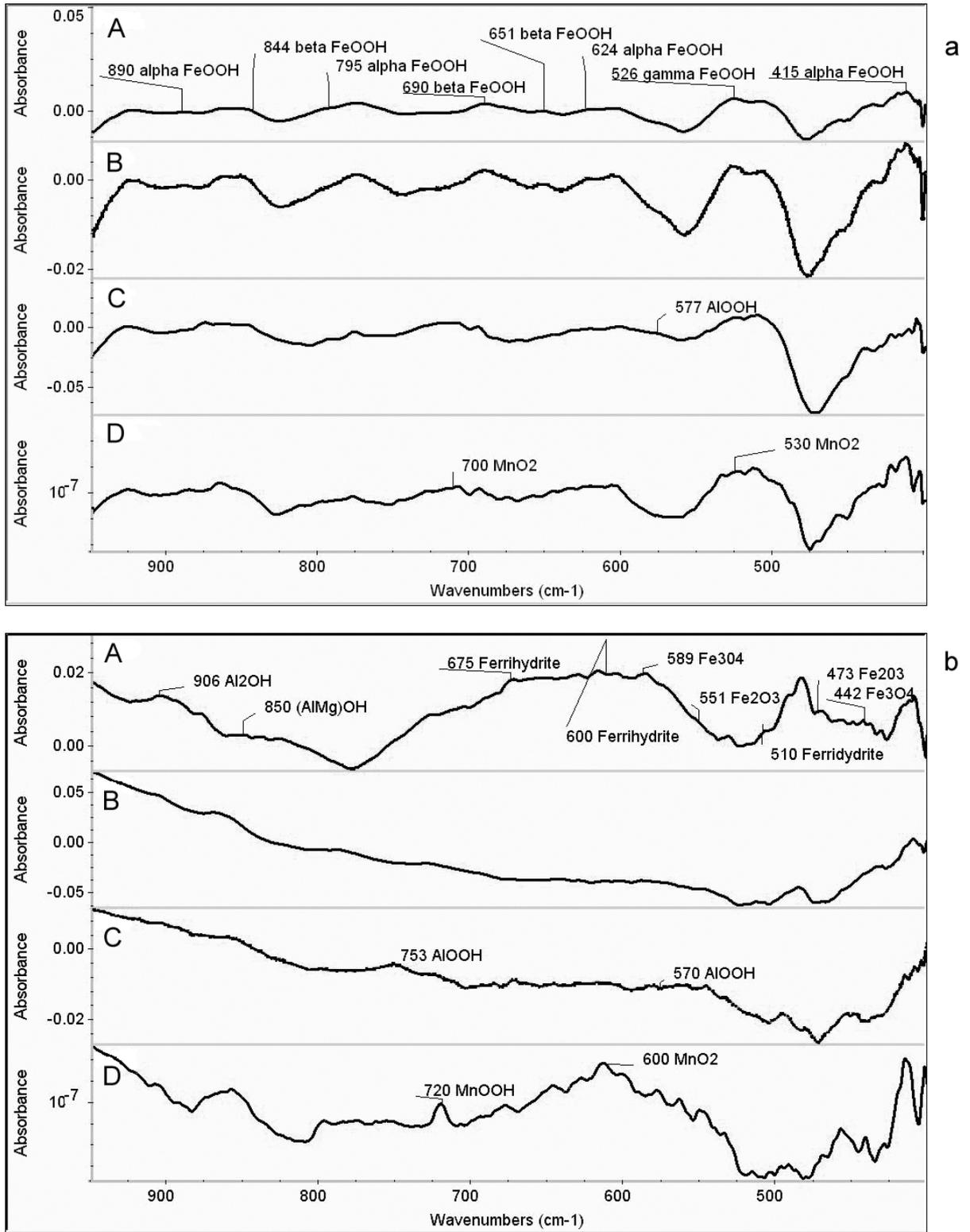
Subtracted infrared spectra in Figure 2 and voltametric curves in Figure 3 illustrated the variability in the metal oxide phases arisen on the solid surface, depending on the carrier and the treating process. Two different type of materials, K1 (Figs. 2a, 3) and BT (Figs. 2b, 3) were investigated by

above mentioned methods. In the case of  $\text{Fe}^{\text{II}}$  treatment, the originally present  $\text{Fe}_2\text{O}_3$  particles and various  $\text{FeOOH}$  phases grew in K1, while in the reactive interlayer of BT,  $\text{Fe}^{\text{III}}$  species were formed. These species were characteristic to  $\text{Fe}^{\text{III}}$  pre-treated montmorillonite (MO), too (Grygar et al., 2007). Generally, the  $\text{Fe}^{\text{III}}$  treatment of investigated clay carriers produced ferrihydrite. After  $\text{Mn}^{\text{II}}$  pre-treatment, different metal oxide species were formed on the solid surface, mainly  $\text{Mn}^{\text{III/IV}}$  oxides on K1 and  $\text{Mn}^{\text{III}}$  oxides on BT. The  $\text{Al}^{\text{III}}$  modification proceeded in a similar manner as  $\text{Fe}^{\text{III}}$  one; hydrolyzed metal particles in a treating solution have been coagulated to  $\text{AlOOH}$  aggregates (see Figs. 2a, 2b).

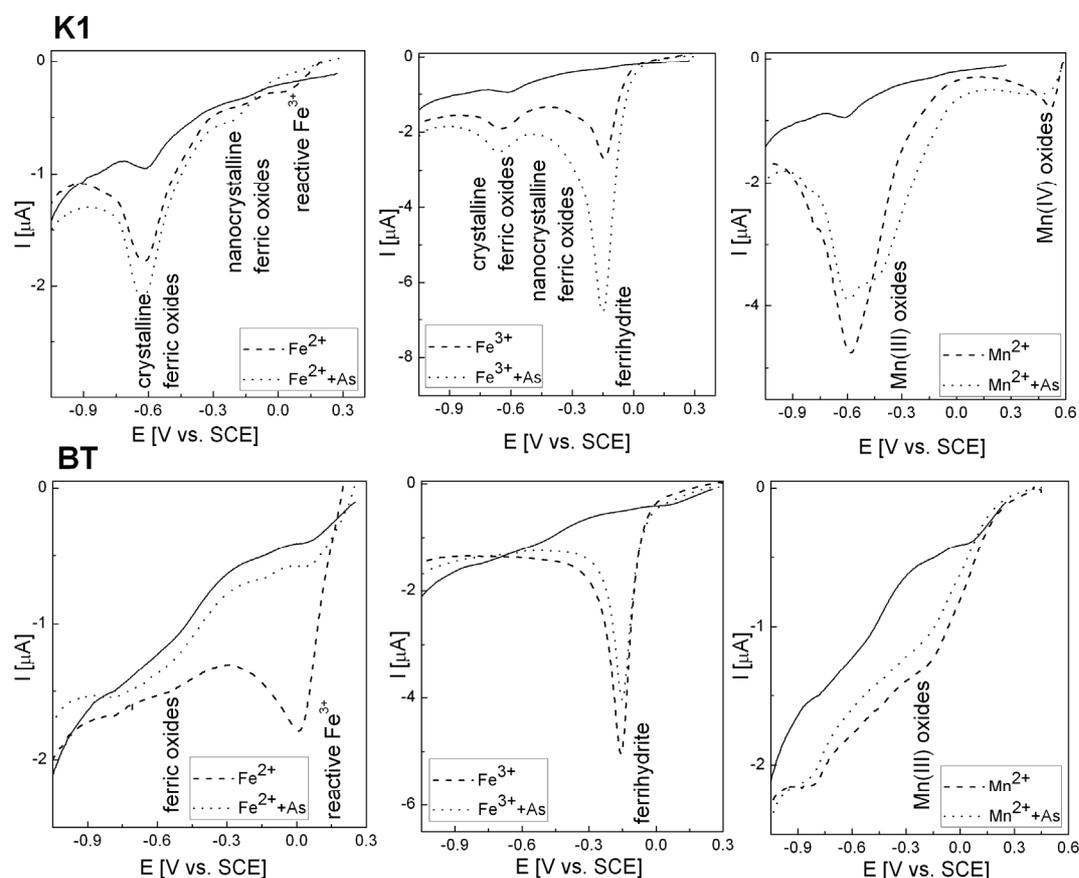
The various forms of hydrated metal phases growing on the carrier surface demonstrated a strong influence of clay type on the treating procedure and equilibrium state, hence the different treating processes have been more or less effective for particular raw material. The hydrolyzed  $\text{FeOOH}/\text{AlOOH}$  aggregates originated from  $\text{Fe}^{\text{3+}}/\text{Al}^{\text{3+}}$  salt solutions were much more suitable for layered carriers with a higher specific surface (MO, BT), whereas in the case of metakaolins (K1, K2) an inhibiting steric effect was observed (Doušová et al., 2006). The small single particles arisen in  $\text{Fe}^{\text{2+}}/\text{Mn}^{\text{2+}}$  salt solutions seemed to be applicable to all investigated aluminosilicates.

### 3.3. THE SORPTION EFFICIENCY OF MODIFIED ALUMINOSILICATES

In all investigated systems the sorption efficiency of raw aluminosilicates did not exceed 20 % (Doušová et al., 2006), while after the metal pre-treatment it varied from 30 to 99 % depending on the



**Fig. 2** Subtracted IR spectra of pre-treated sorbents characterizing new metal phases on solid surface; (a) K1, (b) BT; modification with: Fe<sup>III</sup> (A), Fe<sup>II</sup> (B), Al<sup>III</sup> (C), Mn<sup>II</sup> (D).



**Fig. 3** Voltammetric curves of pre-treated sorbents before- and after As sorption.

**Table 2** Adsorption capacity  $q$  and adsorption efficiency  $\varepsilon$  of prepared sorbents for As removal.

sorbent	modification	$\text{As}^{\text{V}}$ (*)		$\text{As}^{\text{III}}$ (*)	
		$q$ ( $\text{mg}\cdot\text{g}^{-1}$ )	$\varepsilon$ (%)	$q$ ( $\text{mg}\cdot\text{g}^{-1}$ )	$\varepsilon$ (%)
K1,K2	$\text{Fe}^{\text{II}}$	10-12	>98	2	30
	$\text{Fe}^{\text{III}}$	<2	28	2-3	35
K2	$\text{Al}^{\text{III}}$	-	-	>1-2	48->95
	$\text{Mn}^{\text{II}}$	-	-	<2	>97
BT	$\text{Fe}^{\text{II}}$	>4	88	>2	42-99
	$\text{Fe}^{\text{III}}$	$\approx 4$	98	3-4	98-99
	$\text{Al}^{\text{III}}$	-	-	$\approx 4$	>98
CL	$\text{Mn}^{\text{II}}$	-	-	$\approx 5$	>97
	$\text{Fe}^{\text{II}}$	11-16	95-98	<2	24
MO	$\text{Al}^{\text{III}}$	<4	35	<2	20
	$\text{Fe}^{\text{II}}$	6	99	2	49
	$\text{Fe}^{\text{III}}$	9.4	>99	7.8	97
	$\text{Al}^{\text{III}}$	6	99	1.5	42
	$\text{Mn}^{\text{II}}$	-	-	-	-

(\*) initial As concentration  $5 \times 10^{-4} \text{ mol}\cdot\text{l}^{-1}$  for K2, MO;  $2 \times 10^{-3} \text{ mol}\cdot\text{l}^{-1}$  for K1, CL, BT

**Table 3** Adsorption capacity  $q$  and adsorption efficiency  $\epsilon$  of prepared sorbents for Se removal.

sorbent	modification	Se <sup>IV</sup> (*)		Se <sup>VI</sup> (*)	
		$q$ (mg.g <sup>-1</sup> )	$\epsilon$ (%)	$q$ (mg.g <sup>-1</sup> )	$\epsilon$ (%)
K2	Fe <sup>II</sup>	5.5-6.1	90-96	3-4	46-48
	Fe <sup>III</sup>	5.7-6.1	91-99	3-4	54-66
	Al <sup>III</sup>	<6	98-99	4-5.5	73-95
	Mn <sup>II</sup>	4.5-<6	>77-98	<0.5	6-12
CL	Fe <sup>II</sup>	>11	91	<6	41
	Al <sup>III</sup>	<4	20	≈1	11
MO	Fe <sup>II</sup>	7	96	3	44
	Fe <sup>III</sup>	12.1	99.5	6.1	98.5
	Al <sup>III</sup>	-	-	-	-
	Mn <sup>II</sup>	-	-	-	-

(\*) initial Se concentration  $5 \times 10^{-4}$  mol.l<sup>-1</sup> for K2, MO;  $2 \times 10^{-3}$  mol.l<sup>-1</sup> for CL

treating method, raw material and/or the quality of treated solution, i.e. the concentration of toxic oxyanion, pH, additional solved particles, which could behave as competitors, etc. During the adsorption process the majority of highly reactive ion-exchangeable sites on the sorbent surface were stabilized in inner-sphere/outer-sphere surface complexes and unoccupied sites tended to transform to more stable and/or crystalline mineral phases of appropriate metal, such as goethite, boehmite, manganite (Burlinson and Penn, 2006; Masih et al., 2007). The important experimental data for different adsorption systems were summarized in Tables 2 and 3.

The obtained results from Tables 2 and 3 demonstrated strong differences among modified materials and/or sorption procedure, hence the most effective pre-treatment should be tested separately for each investigated system. The percentage value of adsorption efficiency characterized directly the adsorption run, whereas the adsorption capacity related to initial concentration of adsorbed anion. In low concentrated solutions the active surface sites have never been fully saturated, which approved the limited sorption capacities of used sorbents.

Except Fe<sup>III</sup> pre-treated K1, as well as Al<sup>III</sup> pre-treated CL, all prepared sorbents proved high selectivity for As<sup>V</sup>/Se<sup>IV</sup> removal. As<sup>III</sup> and Se<sup>VI</sup> oxyanions have been generally worse adsorbed due to the different type of surface binding (outer-sphere complexes), therefore their effective removal depended on a pre-treating method much more considerably.

#### 4. CONCLUSIONS

Aluminosilicates are not the selective sorbents of anionic contaminants, however, their simple pre-treatment with Fe, Al and Mn salts enabled to prepare anion-active sorbents with high sorption efficiency (> 95 %). A raw material then served as the carrier of hydrated metal oxides layer, which created

active anion exchangeable adsorption sites on the solid surface. The above described methods opened new possibilities of effective and cheap decontamination of As/Sb/Se polluted aqueous systems with the use of low-grade, even waste aluminosilicates. Importantly, different treating methods did not prove the same effect on all investigated materials depending on the structure of raw material (steric properties, specific surface, surface charge).

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