ADSORBENTS FOR IRON REMOVAL OBTAINED FROM VERMICULITE

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ABSTRACT
In presented work, raw, expanded and acid treated vermiculites were used as low-cost and active adsorbents for reducing of environmental pollution with heavy metals. Acid treatment was performed at elevated temperature (95°C) for 2 and 24 h in solution of HNO_3. Adsorption capacity towards Fe^{3+} was studied in column, semi-batch and batch mode. It was shown that all samples are effective in removal of heavy metals; however adsorption mechanism is based not only on ion exchange of interlayer cations but also precipitation/deposition processes. Starting material and modified samples as well as spent adsorbents were characterized with respect to the vermiculite structure using X-ray diffraction method.

KEYWORDS: vermiculite, acid treatment, iron removal, adsorption

1. INTRODUCTION

The quality of water is essential to the maintenance of a healthy hydrological environment and to human health. In accordance to the water framework directive 2000/60/CE and subsequent changes, 2006/11/CE and 2008/32/CE (EU Water Framework Directive), emissions of priority substances should be eliminated. There are two groups of water pollutants of particular interest: refractory organic compounds and heavy metals. During past decades, several physical, chemical and biological methods for pollutants neutralization have been developed. Nevertheless, all of them have their inherent advantages and drawbacks.

Heavy metals, usually present in industrial wastewaters, are toxic, non-biodegradable, and may be bio-accumulated in living tissues. Among different technologies currently coagulation and flocculation are used frequently. Combined with flotation and filtration (electrofiltration, electrochemical processes, precipitation, etc.) they are simple and economically acceptable methods. However, accumulation of concentrated sludge creates a disposal problem as well as high initial cost, high maintenance and operational cost. High consumption of chemicals may result in secondary pollution problem. Precipitation of metal hydroxides or sulfides, besides of large volumes of low density sludge, may be problematic in a mixture of amphoteric metals and in presence of chelating agents. In the case of sulfides, precise regulation of pH is required due to possibility of toxic H_2S

evolution. Application of biological treatment, which is the most publicly acceptable and economical method, is limited because of technical constrains. It requires large area, process is slow, operational flexibility is low and maintenance – complicated. Moreover, microorganisms have high nutrition requirements and xenobiotic molecules cannot be totally degraded. Physical methods, such as membrane-filtration, reverse osmosis and electro-dialysis are usually based on very expensive materials, and cannot handle large volumes of waste-water. The weakness of the aforementioned methods is also high power consumption. On the other hand, another physical process – adsorption is much more effective and economical. Facing more and more stringent environmental regulations, new waste-free techno-logies must be developed, based on cheaper, non-toxic materials. Clays proposed as starting materials fulfill all requirements for low-cost, ecological precursors for industrial technologies or large scale applications (Fu and Wang, 2011; Crini, 2006; Forgacs et al., 2004; Sumathi et al., 2005).

Vermiculite is natural clay mineral with layered structure. It consists of octahedral alumina or magnesia sandwiched between two tetrahedral silicate sheets. Net negative charge is compensated by interlayer cations such as K^+, Mg^{2+}, Fe^{3+}. Due to low cost and availability raw mineral has been exploited in many applications: accumulation of water, adsorption of heavy metals, oil, humic acids and pesticides (Vieira dos Santos and Masini, 2007; Abate et al.,
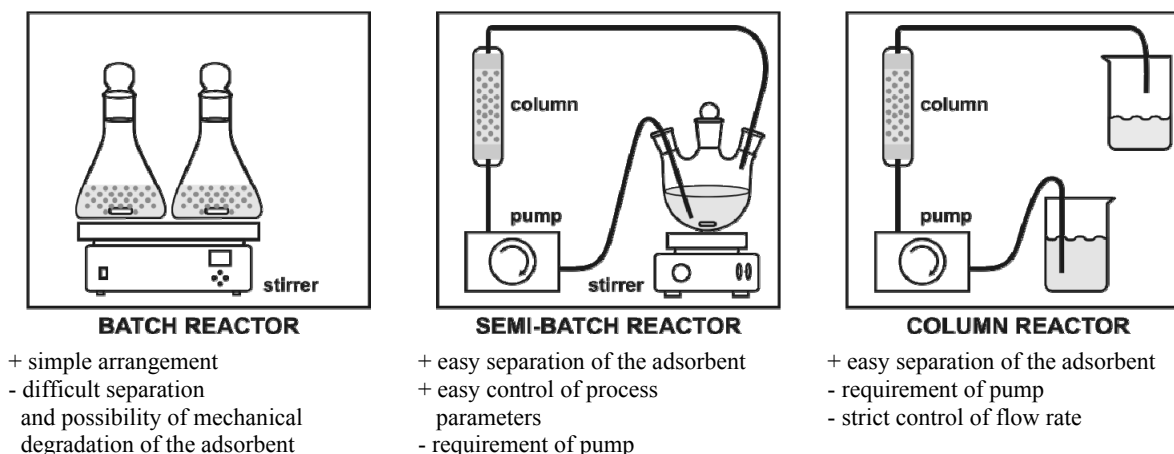
BATCH REACTOR
+ simple arrangement
- difficult separation
  and possibility of mechanical
  degradation of the adsorbent

SEMI-BATCH REACTOR
+ easy separation of the adsorbent
+ easy control of process
  parameters
- requirement of pump

COLUMN REACTOR
+ easy separation of the adsorbent
- requirement of pump
- strict control of flow rate

Fig. 1 Experimental set-up for adsorption in batch, semi-batch and column mode.

2006; Malandrino et al., 2006; da Fonseca et al., 2005). However, as it is in the case of other clays and clay minerals, many techniques, such as: pillaring with polycations, modification with organic compounds or selective leaching, were proposed to improve chemical properties of the mineral, its morphology and texture both for applications in catalysis and adsorption (Abate et al., 2006; Machado et al., 2006; Zhao et al., 2008; Chmielarz et al., 2009; Yu et al., 2010).

The research data suggest that mechanism of heavy metal removal from waste waters using vermiculite is governed by ion exchange. The process efficiency may be also influenced by the presence of other cations and ligands (Malandrino et al., 2006; da Fonseca et al., 2006; Abollino et al., 2008; El-Bayaa et al., 2009). In presented work another hypothesis of possible adsorption mechanism is tested – deposition/precipitation of polymeric species on the surface and in interlayer galleries. In presented work solution containing Fe^{3+} was used as a model adsorbate for heavy metals removal process.

2.   EXPERIMENTAL
2.1. MATERIALS AND CHARACTERIZATION

Commercial raw (VA0) and expanded (VAe0) vermiculite (South Africa), fraction size 1 mm, was provided by Romico Polska Sp. z o.o. Expanded vermiculite was used as a starting material for preparation of acid modified samples according to the following procedure:

- 100 mL of 0.8 M HNO_3 was placed in round-bottom flask equipped with reflux condenser and its temperature was raised to 95 °C,

- 10 g of vermiculite (VAe0) was added to hot solution of acid and kept stirring at elevated temperature for 2 or 24 h (sample names: VAeN2 and VAeN24, respectively),

- vermiculite flakes were filtered and washed with distilled water, then both samples were dried at room temperature.

The structure of raw, expanded and acid treated as well as spent samples was studied using X-ray powder diffractometer (Bruker, D2 PHASER) equipped with CuK_α radiation source.

2.2. ADSORPTION EXPERIMENTS

Adsorption of Fe^{3+} as a model metal cation was studied in 3 different modes: batch, semi-batch and column (Fig. 1). In all experiments sample VAe0 was used as received from company, additionally in semi-batch and column experiments adsorbent was diluted (1:10) with quartz sand. The following parameters were set for experiments:

- concentration range: 0.00012-0.002 mol Fe^{3+}/L,

- flow rate: semi-batch 100 mL/min, column 2.8-2.4 mL/min,

- solution/adsorbent ratio: batch/semi-batch: 200 mL/0.25 g, column: 400 ml/0.25 g,

- temperature: 25 °C,

- pH = 3.5 (adjusted with acetate buffer).

In batch mode experiments with different adsorbents were performed at the following conditions:

- samples: VA0, VAe0, VAeN2, VAeN24,

- concentration range: 0.0015-0.0054 mol Fe^{3+}/L,

- solution/adsorbent ratio: batch: 100 mL/0.125 g,

- temperature: 25°C

- pH = 3.5, acetate buffer 0.2 M.

3.   RESULTS AND DISCUSSION
3.1. CHARACTERIZATION OF FRESH ADSORBENTS

The X-ray diffraction (XRD) patterns of all adsorbents are presented in Figure 2. The intensity of recorded peaks of raw vermiculite (VA0) was decreased 10 times to make easier comparison between all samples. Natural raw vermiculite – as received from the company, is characterized with highly ordered structure. All reflections are sharp and
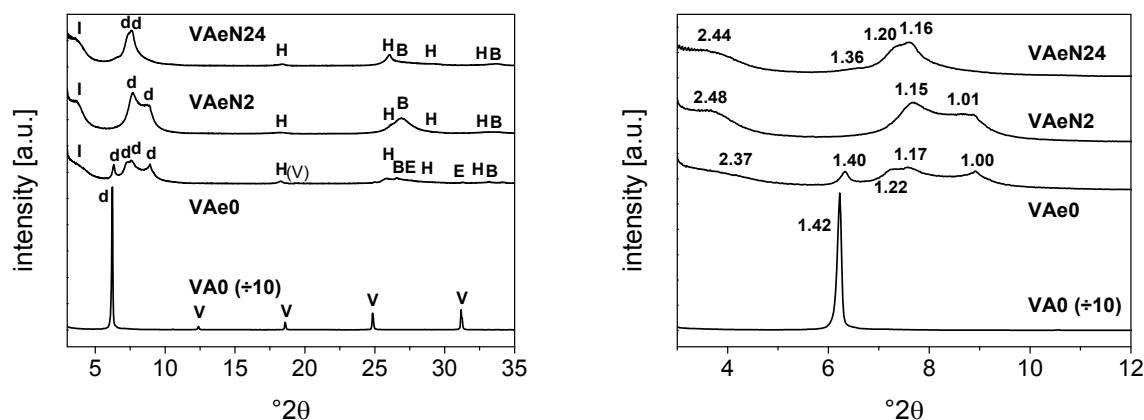
Fig. 2 XRD patterns of raw (VA0), expanded (VAe0) and acid treated (VAeN2, VAeN24) vermiculites; I-interstratified phase, H - hydrobiotite, B - biotite, V - vermiculite:, E - enstatite, d – basal reflections.

Table 1 Interlayer distances of raw (VA0), expanded (VAe0) and acid treated (VAeN2, VAeN24) vermiculites.

| sample name	d [nm]	d [nm]	d [nm]	d [nm]	d [nm]
VA0	-	1.42	-	-	-
VAe0	2.37	1.40	1.22	1.17	1.00
VAeN2	2.48	-	-	1.15	1.01
VAeN24	2.44	1.36	1.20	1.16	-
	inter-stratification	2 layers of water Mg^{2+}/Fe^{3+}	inter-stratification	1 layer of water Mg^{2+}/Fe^{3+}	0 layers of water H_3O^+ (K^+)

very intense and confirm presence of vermiculite (Gordeeva et al., 2002; da Fonseca et al., 2006; Marcos et al., 2009). No side-phases or impurities were identified. On the contrary, expanded material (VAe0) is characterized with complex phase composition. Two main phases were identified: hydrobiotite (peaks of high intensity at 1.223, 0.349, 0.491, 0.272 nm) (Downs, 2006) and biotite (peaks of high intensity at 1.01, 0.337, 0.266 nm) (Downs, 2006). Probably traces of vermiculite could be also detected as well as enstatite. Moreover, it cannot be excluded that mica-like structure, probably muscovite, was formed (Marcos et al., 2009; Marcos et al., 2010). In acid treated samples both hydrobiotite and biotite were also identified, although the former phase is dominating in the sample treated for longer time (VAeN24) and the latter one in the sample treated only for 2 h (VAeN2). It cannot be excluded that material contains also amorphous silica which is formed due to leaching of phyllosilicale layers (Chmielarz et al., 2010; Chmielarz et. al., 2012).

In each sample several basal reflections were identified (Table 1.). In the case of raw vermiculite VA0 calculated interlayer space value was indicating the presence of 2 layers of water, characteristic for such cation as Mg^{2+} or Fe^{3+} (Helsen, 1975; Argüelles et al., 2011). For expanded vermiculite the presence of 2, 1 or 0 layers of water molecules in the domains of the layered structure is typical. In acid treated samples diversity of basal spacings is limited due to successful ion exchange for hydronium cations (Chmielarz et al., 2010; Chmielarz et. al., 2012). However, it should be noted that extensive acid treatment results in dissolution of octahedral sheet and released cations may also occupy interlayer galleries.

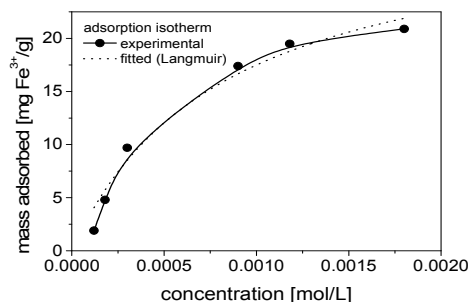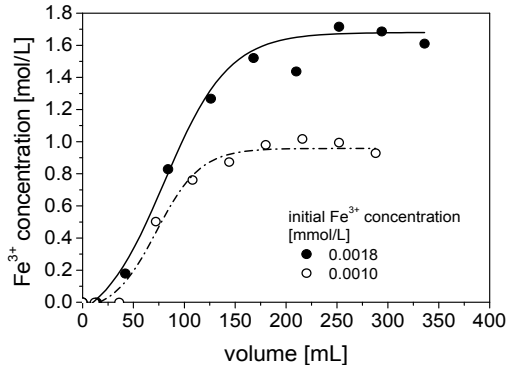### 3.2. ADSORPTION IN BATCH, SEMI-BATCH AND COLUMN MODE

All the performed experiments showed that expanded vermiculite adsorbs significant amount of Fe^{3+}. Kinetic curves for each type of set-up are presented in Figure 3. In batch/semi-batch experiments only at low Fe^{3+} concentrations equilibrium was reached in 120 minutes (total time of adsorption). At higher concentrations adsorbed amount was still increasing. Both isotherms presented in Figure 3. show that monolayer coverage has been not reached. Also in the case of column experiment at higher concentration full saturation of adsorbent is questionable after feeding about 350 mL of the solution containing Fe^{3+} cations. The best method, resulting in highest removal degree and easy operation was semi-batch method. Based on estimated adsorption capacities, it might be concluded that in order to reach higher level of purification a combination of batch or semi-batch mode with column mode might be employed. Semi-batch and batch modes perform better with higher concentrated

BATCH
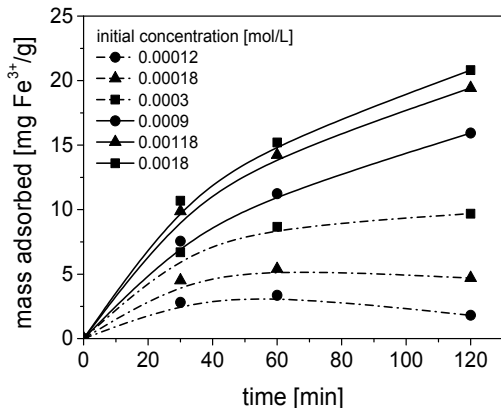
BATCH
adsorption capacity (2 h):
21 mg Fe^{3+}/g, 0.376 mmol Fe^{3+}/g
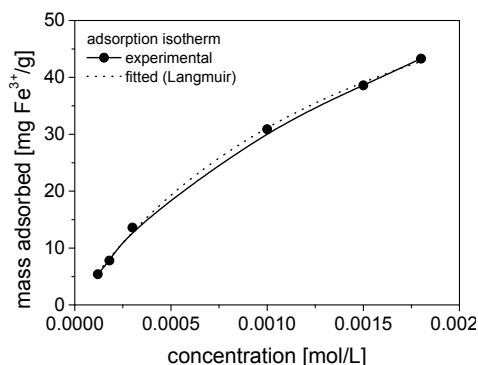
SEMI-BATCH
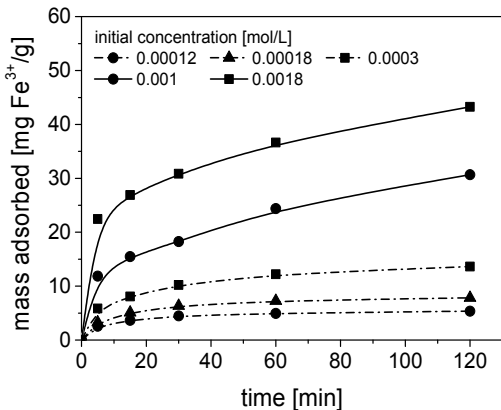
SEMI-BATCH
adsorption capacity (2 h):
45 mg Fe^{3+}/g, 0.806 mmol Fe^{3+}/g

COLUMN

COLUMN
adsorption capacity
(at concentration 0.0018 mol/L):
32 mg Fe^{3+}/g, 0.58 mmol Fe^{3+}/g

Fig. 3 Results of iron adsorption on expanded vermiculite VAe0: kinetic curves of Fe^{3+} adsorption on expanded vermiculite for batch, semi-batch and column mode (left); isotherms and maximum adsorption capacities measured for the sample VAe0 (right).

solutions, thus they would be used as a pre-treatment unit. The process would be then accomplished in column which work is satisfactory with relatively low concentrated solutions. However, batch mode is less desired option than semi-batch, because in batch mode additional separation equipment is required before entering the column – that makes the process more expensive.

3.3. COMPARISON OF PROPERTIES OF DIFFERENT ADSORBENTS

A series of batch experiments was performed in order to compare adsorption properties of raw (VA0), expanded (VAe0) and acid treated (VAeN2, VAeN24) vermiculites (Fig. 4). Based on previous measurements broader range of concentrations as well as longer adsorption time was applied - concentration of
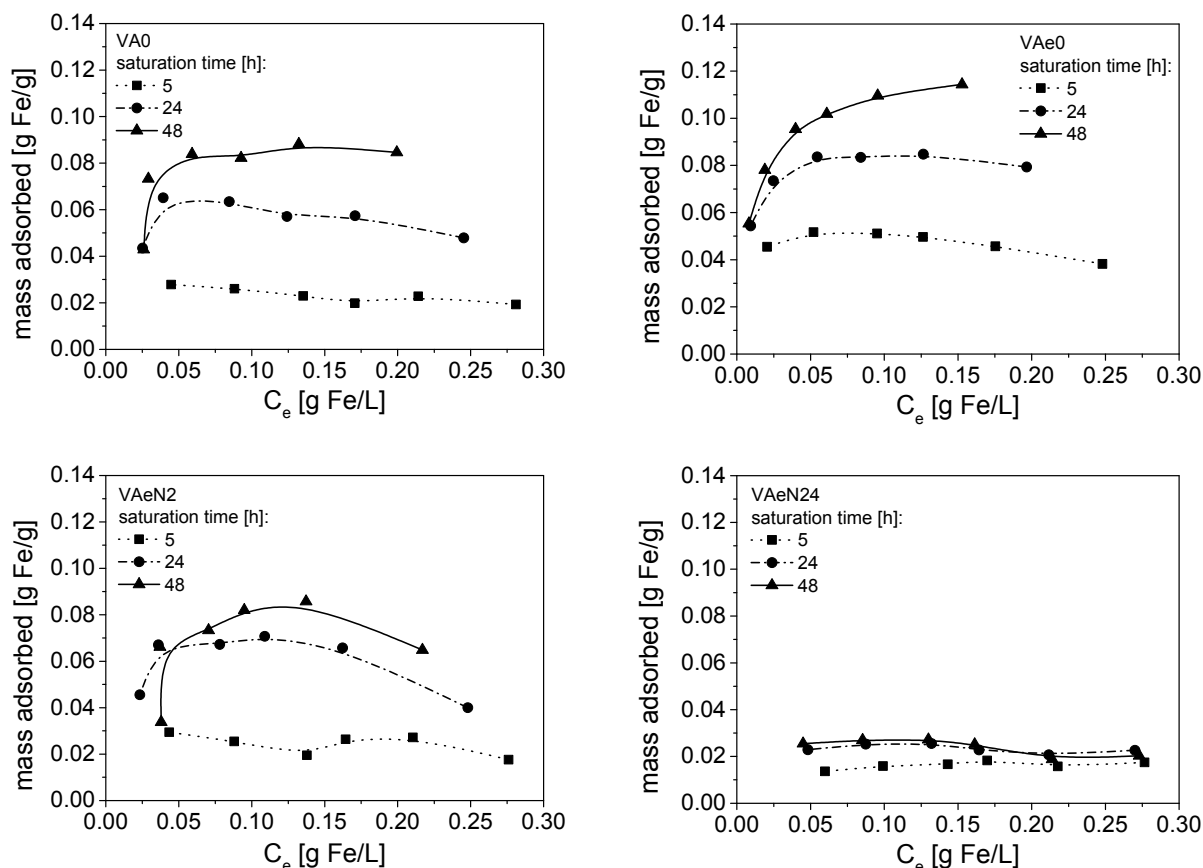
Fig. 4 Adsorption isotherms obtained on raw (VA0), expanded (VAe0) and acid treated (VAeN2, VAeN24) vermiculites.

Fe^{3+} was measured at 5, 24 and 48 h. It was observed that equilibrium was not reached. The amount of Fe^{3+} adsorbed on raw and expanded vermiculite and also on the sample treated with acid for 2 h is increasing in consecutive measurements. It was also demonstrated (Fig. 4, high concentration range for the samples VA0, VAe0, VAeN2) that adsorption strongly depends on initial concentration of adsorbate. Surprisingly, in almost all experiments increase of initial iron concentration resulted in decreased content of adsorbed Fe^{3+}. It should be stressed that each batch contained constant volume of buffering solution. Nevertheless, it should be taken into account that dissolved Fe^{3+} salt made significant contribution to ionic strength of the mixture. Thus, hydrolysis of Fe^{3+} cannot be excluded and may influence adsorption mechanism.

It was reported before that vermiculites are characterized with high adsorption properties (Bergaya et al., 2006; Abollino et al., 2008; Abollino et al., 2007) and adsorption mechanism is determined by cation exchange capacity. However, for such metal cations as Cu^{2+} or Ni^{2+} it was proven using X-ray absorption fine structure (EXAFS) spectroscopy and X-ray absorption near edge spectroscopy (XANES)

that inner-sphere and outer-sphere complexes are formed and adsorption takes place on the edges of vermiculite (Furnare et al., 2005; Yang et al., 2011). On the other hand, Scheinost and Sparks (Scheinost and Sparks, 2000) suggested that α-type (metastable) metal hydroxides of Co and Ni were formed in the presence of the minerals such as montmorillonite and vermiculite. Surface precipitates may not be attached to the sorbent and Ni and Co-containing precipitates were formed within short reaction times (minutes to days). Described phenomenon was observed even when the calculated surface coverage was below a monolayer, and the pH was below saturation with respect to the known solubility products (solubility constants) of β-type hydroxides. As a result formation of a phyllosilicate with one or two silica sheets sandwiching a metal hydroxide sheet can be observed. Furthermore, easy formation of Al- or Fe- hydroxy interlayers (chlorite-like structures) in laboratory conditions was claimed by several authors (Carstea, 1968; Sawhney, 1968; Saha and Inoue, 1998), although time required for the reaction was relatively longer (days to weeks). All species that participate in adsorption mechanism are presented in Figure 5.
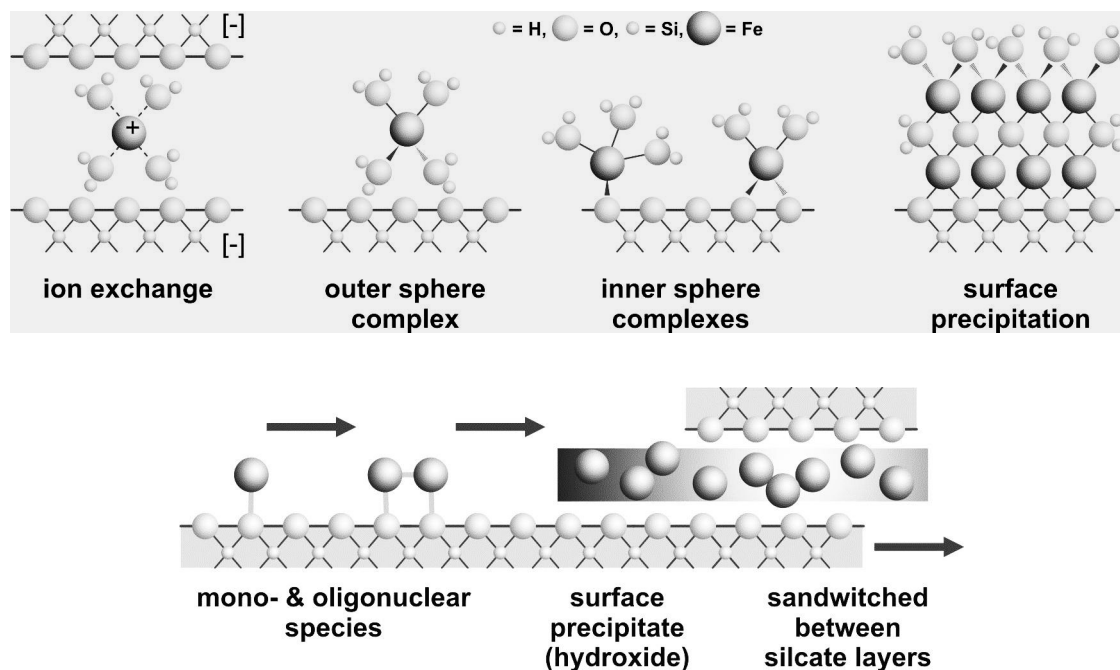
Fig. 5 Species of proposed adsorption mechanisms on vermiculite-based adsorbents.

Additional data support suggested mechanism. Typically CEC of vermiculites is in the range of 130-210 meq/100 g. Thus, one can expect that maximum amount of metal cations exchanged would not be higher than 2.1 mmol of positive charge per 1 g. However, results obtained for 4 different vermiculites (Fig. 6) are equal: 0.912-2.730 mmol [+]/g after 5 h, 1.365-4.512 mmol [+]/g after 24 h and 1.467-6.123 mmol [+]/g after 48 h. Only in the case of acid treated sample VAeN24 calculated values do not exceed potential cation capacity. But it should be stressed that in acid treated samples CEC is lower due to removal of octahedral sheet and reduced layer charge.
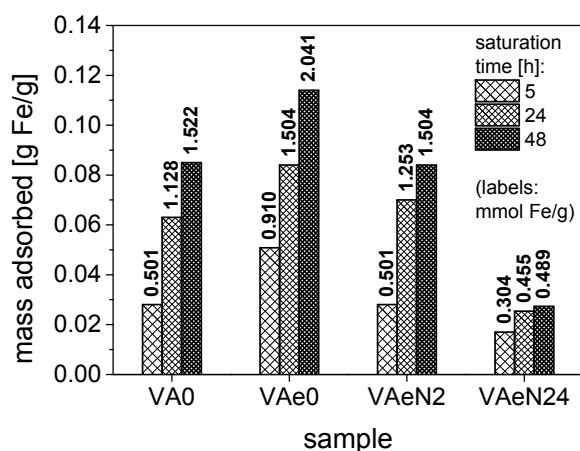

Fig. 6 Maximum adsorption capacities towards Fe^{3+} obtained on raw (VA0), expanded (VAe0) and acid treated (VAeN2, VAeN24) vermiculites.

3.4. CHARACTERIZATION OF SPENT ADSORBENTS

Characterization of spent adsorbents was performed for the samples digested in adsorbate solution for 48 h at concentration 0.0054 mol Fe^{3+}/L (sample names VAxFe1). XRD studies confirmed that modified adsorbents structure has been altered upon adsorption process. Diffraction patterns in Figure 7 revealed that expanded vermiculite (VAe0) which consisted of the mixture of domains with 0, 1 and 2 water layers in layered structure was transformed successfully into vermiculite phase with two-one layer water and Fe^{3+} cations intercalated in interlayer space.

In the case of expanded and additionally acid treated sample VAeN2 changes were noticeable mostly in the range of basal reflections. Intercalation of Fe^{3+} occurred and peak associated with the presence of 2 layers of water appeared. However the structure reconstruction was not as spectacular as for expanded material. Phases of mica-like phase with no water molecules in the interlayer can be distinguished and they are overlapping with vermiculite reflections. Intercalation of cations was probably inhibited due to reduced layer charge as a result of acid treatment. It cannot be excluded that amorphous silica formed as a result of acid treatment, also hinders intercalation and adsorption process.

On the contrary, in raw vermiculite it is difficult to observe any changes – basal reflections remain unaffected. This is understandable since Mg^{2+} cations give rise to the same arrangement of water molecules as Fe^{3+}. The only change observed was decrease of intensity of peaks between 10 and 35°2θ. Calculated basal spacings are shown in Table 2.
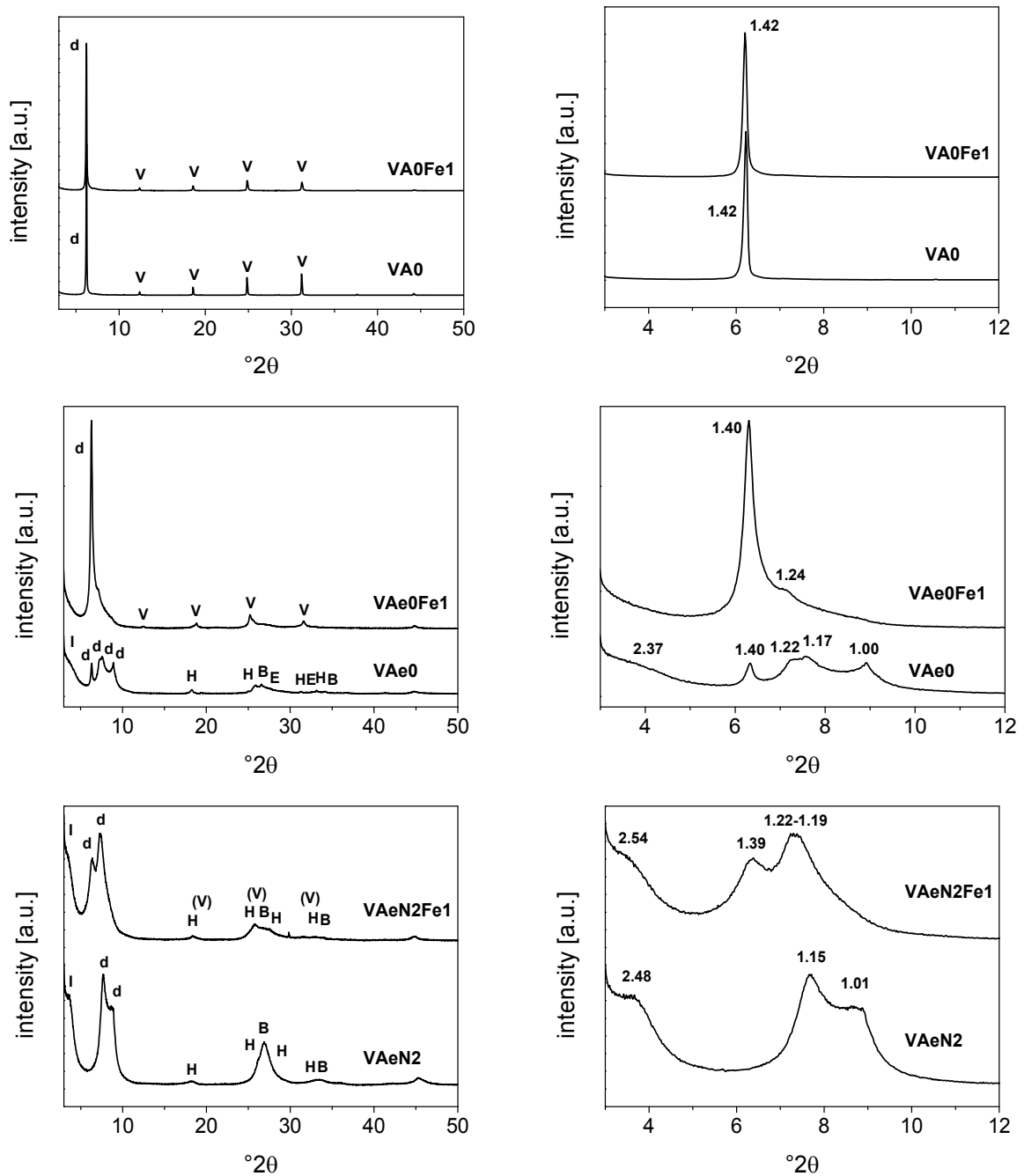
Fig. 7 XRD patterns of spent vermiculite-based adsorbents (VAxFe1); I- interstratified phase, H – hydrobiotite, B - biotite, V – vermiculite, E - enstatite, d – basal reflections.

Table 2 Interlayer distances of spent vermiculite-based adsorbents (VAxFe1).

sample name	d [nm]	d [nm]	d [nm]	d [nm]	d [nm]
VA0Fe1	-	1.42	-	-	-
VAe0Fe1	-	1.40	1.24	-	-
VAeN2Fe1	2.54	1.39	1.22	1.19	-
	inter-stratification	2 layers of water Mg^{2+}/Fe^{3+}	inter-stratification	1 layer of water Mg^{2+}/Fe^{3+}	0 layers of water H_3O^+ (K^+)

Furthermore, it was impossible to identify precipitation products such as iron oxides/hydroxides in any of studied samples after adsorption because they are characterized with low crystallinity and a small mass compared to the adsorbents.

4. CONLUSIONS

In presented work it was shown that vermiculite-based adsorbents have great potential in application of water and wastewater purification. Modifications such as expanding or acid treatment are beneficial for the adsorption, however in the latter case mild conditions are preferred. Further studies are necessary to evaluate the influence of acid treatment for removal contaminants such as dyes or pesticides (in general organic molecules). In designing of suitable adsorbent it should be taken into account that heavy metals usually are accompanied by other contaminants.

Higher efficiency of purification can be achieved in a combination of batch or semi-batch mode with column mode. Semi-batch and batch modes perform better with higher concentrated solutions, thus they would be used as a pretreatment unit, and the process would be then accomplished in column which work is satisfactory with relatively low concentrated solutions. Batch mode is less desired option than semi-batch, because additional separation equipment is required before entering the column.

It was shown that obtained adsorption capacities are higher than typically measured cation exchange capacities. Thus, we can expect that formation of inner and outer sphere complexes as well as surface precipitates and hydroxyl interlayers may contribute in the adsorption mechanism.

The structure of modified samples was altered significantly. Expanded material was reconstructed into vermiculite phase and acid treated sample was intercalated with Fe^{3+} cations. However, it was impossible to identify Fe^{3+} precipitates such as oxide or hydroxide phases.

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