Sorption of V and VI group metalloids (As, Sb, Te) on modified peat sorbents

DOI: 10.1515/chem-2016-0003
received October 29, 2015; accepted January 18, 2016.

Abstract: The present work investigates arsenic, antimony and tellurium sorption using iron modified peat. The results were obtained using batch tests and the sorption was studied as a function of initial metalloid concentration, pH and sorption time, as well as the presence of competing substances. The obtained results indicate that modification of peat with Fe compounds significantly enhances the sorption capacity of the sorbents used for sorption of arsenic, antimony and tellurium. The optimal pH interval for the sorption of Sb(III) is 6.5–9 and for As(V) and Sb(V) – 3–6, while As(III) and tellurium sorption using Fe-modified peat is favourable in a wider interval of 3–9. The presence of competing ions as well as HA affect sorption of metalloids on Fe-modified peat. A minor impact on the reduction of metalloid sorption was detected in the presence of nitrate, sulphate, carbonate and tartrate ions, while in the presence of phosphate and HA the sorption ability of metalloids can be considerably reduced. The obtained results of kinetic experiments indicate that sorption of metalloids on Fe-modified peat mainly occurs relying on mechanisms of physical sorption processes.

Keywords: peat, sorbents, arsenic, antimony, tellurium, metalloids

1 Introduction

Nowadays, growing attention is being paid to environmental pollution with metalloids (As, Sb, Te) [1-5]. Due to the wide distribution and toxicity, arsenic is the most studied metalloid. At the same time, considerably lower attention has been paid the research of antimony and tellurium. However, it is important to study the occurrence of antimony and tellurium in the environment as well as associated environmental pollution and possible solutions for environmental remediation.

Arsenic is a well-known toxic element that can be found in drinking water in problem areas, for example, in SE Asia. The concentration of arsenic in these areas exceeds maximal permissible levels several times [4,6-8]. Arsenic can enter into natural water systems through a range of natural as well as anthropogenic sources. Weathering of rocks and minerals containing arsenic, volcanic emissions and also a result of some biological processes can be mentioned as example of natural processes releasing arsenic into the environment. Moreover, anthropogenic sources include release of arsenic from various industries, such as smelting, petroleum refinery, glass manufacturing, production of fertilizers, and intensive application of arsenic containing plant protection chemicals such as insecticides, herbicides and crop desiccants, as well as arsenic additives are used in the production of livestock feed [9-11].

Arsenic exists in four oxidation states: -3, 0, +3, and +5, and it can be found in both inorganic and organic speciation forms. The inorganic species of arsenic are more common and toxic than the organic species. Inorganic arsenic is the predominant form found in polluted waters, and it exists...
in two oxidation states – As(III) and As(V), depending on pH and red-ox conditions [1,12]. In media with pH 3–9, the dominant species of As(III) is neutral $\text{HAsO}_3^-$, while those of As(V) are negatively charged $\text{HAsO}_4^{2-}$ and $\text{HAsO}_4^{3-}$ [4].

Antimony, like arsenic, is a toxic element which is present in the environment as a result of natural and human activities. Wide use of antimony in industry is the main anthropogenic source of this element.

The concentration of antimony in unpolluted waters is low, usually less than 1 µg L$^{-1}$, while in polluted areas – close to anthropogenic sources – concentration can be up to 100 times higher in comparison with natural levels [3].

Similarly to arsenic, antimony can exist in a variety of oxidation states: -3, 0, +3, and +5, while mainly in the environment it occurs in inorganic forms – Sb(III) and Sb(V). Like arsenic(V), Sb(V) is the predominant species in oxic systems and Sb(III) in anoxic systems; although some studies reveal that significant amounts of Sb(III) can be also found in oxic and Sb(V) in anoxic systems [3,13].

Up to now, studies on tellurium and distribution of its compounds in the environment are limited, and the main attention in the existing studies has been focused on tellurium pollution near the main tailing and industrial areas [5]. Aqueous Te species mainly exist in the form of oxyanions – tellurite ($\text{TeO}_2^{2-}$) and tellurate ($\text{TeO}_4^{3-}$) or hydroxide anions ($\text{Te(OH)}_2^-$, $\text{TeO(OH)}_2^-$). Te(VI) is the predominant form in aqueous media under oxic conditions, whereas Te(IV) predominates under reducing conditions [14,15].

Different refinement technologies are used to reduce pollution of metalloids, for example, precipitation, sorption, ion exchange, extraction and cementation. Each of these has some advantages and disadvantages. However, the main disadvantage is the high costs. It is considered that sorption is one of the most effective and affordable methods [6-8,10].

Until now, sorbents of different origin, efficiency and costs are used. But recently increasing attention is paid to the sorbents which are made on the basis of natural materials such as waste products of agriculture and food industry [16].

Some previously studied sorbents are effective for sorption of one metalloid form, for example, arsenates, but they are less efficient for sorption of other forms such as arsenites.

Peat can be a perspective material for sorbents. It is a widespread natural material in Northern Europe and elsewhere. The advantages of peat based sorbents are as follows: it is an environmentally friendly sorbent, it is a low cost sorbent and it can be utilized by combustion. Taking into account the affinity of metalloids to interact with Fe-containing compounds, investigation of metalloid sorption can be carried out using iron modified biomaterial sorbents.

The aim of the thesis is to obtain modified peat sorbents, characterise them and investigate V and VI group metalloid (As, Sb, Te) sorption onto modified peat sorbents.

2 Experimental

Analytical quality reagents (Sigma-Aldrich Co., Fluka Analytical, Scharlau, Stanlab, Penta) were used without further purification. High purity water Milliapore Elix 3 (Millipore Co.) 10–15 MΩ cm was used for preparation of solutions.

Disodium hydrogen arsenate heptahydrate (Na$_2$H$_2$AsO$_4$ · 7H$_2$O; Sigma-Aldrich), sodium arsenite (NaAsO$_2$; Fluka), cacodylic acid (C$_4$H$_8$AsO$_3$; Sigma-Aldrich), potassium hexahydroxoantimonate(V) (KSb(OH)$_6$; Fluka), potassium antimony tartrate semi hydrate (C$_6$H$_4$KO$_2$Sb · 0.5H$_2$O; Sigma-Aldrich), potassium tellurite hydrate (K$_2$TeO$_3$ · 0.5H$_2$O; Sigma-Aldrich) and telluric acid (H$_4$TeO$_6$; Sigma-Aldrich) were chemicals of analytical grade. Sorption experiments were provided using three different peat samples modified with Fe(III) hydroxide (Fe-modified peat from the Gagu Bog, Fe-modified peat from the Silu Bog, Fe-modified peat from the Dizais Veikenieks Bog). Peat was derived from three bogs in Latvia: high type cotton grass-sphagnum peat (depth 50–60 cm) from the Gagu Bog, high type peat (depth 12.5–25 cm) from the Silu Bog and high type fuscum peat (depth 25–52 cm) from the Dizais Veikenieks Bog.

Modification of materials involved precipitation of iron hydroxides on the surface of the studied material with the following thermal treatment [6,8]. 6755 g (0.25 mol) FeCl$_3$ · 6H$_2$O were dissolved in 250 mL distilled water, adding 250 mL 3M NaOH and leaving for 4 hours. Then, the formed precipitates were rinsed and decanted in a 1 L vessel. The dispersion of Fe(OH)$_3$ was mixed in 100 g of homogenized peat. After filtration, the reaction product was rinsed with approximately 0.5 L deionized water, filtered, dried and heated for 4 hours at 60°C.

As three different peat samples were used for modification, for their separation the name of peat bog is shown in brackets, e.g., mod. peat (Gagu) – peat sample derived from the Gagu Bog (depth 50–70 cm) modified with Fe(OH)$_3$, followed by thermal treatment.
2.1 Characterisation of sorbents

Characterization of sorbents was done using the Fourier transformation infrared (FT-IR) spectra, scanning electron microscopy (SEM), specific surface area measurements as well as analysis of moisture content, organic substances content and Fe₂O₃.

For determination of organic matter, the loss-on-ignition (LOI) method was used. 1 g of each sample was dried at 105°C temperature for 12 h and then burned at 550°C temperature in a muffle furnace for 4 h. Samples were weighed after cooling, and content of organic matter was calculated according to LOI (Eq. 1.) [17]:

\[ \text{LOI}_{550} = \frac{\text{DW}_{105} - \text{DW}_{550}}{\text{DW}_{105}} \times 100 \]  

(1)

where LOI₅₅₀ – LOI at 550°C (%), DW₁₀₅ – dry weight of the sample before combustion (g), and DW₅₅₀ – dry weight of the sample after heating at 550°C (g).

The content of Fe₂O₃ was determined in samples after heating at 550°C. Samples were mineralized using concentrated HCl and conc. HNO₃, and heated at 120°C for 2 h. In corresponding filtrates after dilution Fe was analysed using an atomic absorption spectrometer with flame atomization (FAAS) (Perkin-Elmer Analyst 200 atomic absorption spectrophotometer). The content of iron(III) oxide in the sorbent was calculated according to the Eq. 2.

\[ w_{\text{Fe}_2\text{O}_3} = \gamma_{\text{Fe}} \times \frac{M_{\text{Fe}} \cdot V}{m} \]  

(2)

where \( \gamma_{\text{Fe}} \) – concentration of iron in the sample (mg g⁻¹), \( M_{\text{Fe}} \) and \( M_{\text{Fe}_2\text{O}_3} \) – molecular weight of Fe and Fe₂O₃ (g mol⁻¹), V – volume of the sample (L), and m – mass of sorbent (g).

Fourier transformation infrared spectra were obtained for all sorbents using a Perkin Elmer Spectrum BX FT-IR spectrometer, and data processing was conducted using Spectrum v 5.3.1 software. Samples were pressed in KBr pellets, and the spectra were recorded in the range of 4000–450 cm⁻¹ with a 4 cm⁻¹ resolution.

SEM data were obtained using a scanning electron microscope JOEL ISM T–200. Samples were measured in the secondary electron regime, with the SEM operating voltage of 25 kV.

The surface area of sorbents was measured using a surface area pore size analyser Gemin2360. The Brunauer–Emmett–Teller (BET) method was used for the specific surface area measurements.

Determination of the point of zero charge (pHₚzc) was provided using an immersion technique [18].

0.03 M KNO₃ was added to 0.5000 g of sorbent. After that solutions were adjusted at different pH values using 0.1 M NaOH and 0.1 M HCl. Aqueous suspensions were agitated for 24 h in a shaker and after that the pH was measured. The change of pH (ΔpH) during equilibration was calculated and the pHₚzc was identified as the initial pH with minimum ΔpH.

Experimentally obtained data were processed with MS Excel. The correlation of obtained sorption data was calculated using the Langmuir and Freundlich isotherm models.

The least square method and MS Excel optimization tool (Solver) were used to obtain theoretical sorption isotherms. The modified Langmuir-1 equation (Eq. 3.) was used for optimization. It was assumed that sorbents have two sorption centres.

\[ q_e = \frac{q_{m1} \cdot k_1 \cdot C_e}{1 + k_1 \cdot C_e} + \frac{q_{m2} \cdot k_2 \cdot C_e}{1 + k_2 \cdot C_e} \]  

(3)

where \( q_e \) – sorbed amount (mg g⁻¹); \( C_e \) – sorbate equilibrium concentration (mg L⁻¹); \( q_{m1} \), \( q_{m2} \), and \( k_1 \), \( k_2 \) – Langmuir constants which are associated with sorption capacity and sorption energy, respectively.

2.2 Sorption experiments

Sorption experiments were conducted using a batch system. Na₃AsO₄ × 7H₂O, Na₃AsO₄, and C₆H₅AsO₃ were used for preparation of arsenic stock solutions at various concentrations of arsenic (300, 200, 100, 50, 25, 10 and 5 mg L⁻¹). K₂S₂O₃ and C₆H₅KO₂Sb × 0.5H₂O were used for preparation of antimony stock solutions at various concentrations of Sb (10, 25, 50, 100, 200, 300, 400, 600, 800, 1000 mg L⁻¹). H₂TeO₃ and K₂TeO₃ × H₂O were used for preparation of tellurium stock solution at such concentrations of Te as 10, 25, 50, 100, 200, 300, 400, 600, 800, 1000 mg L⁻¹.

40 mL of a metalloid solution was added in each 100 mL glass vessel with 0.5 g sorbent. Vessels were shaken for 24 h at room temperature. The suspension was then filtered, and a concentration of metalloid in the filtrate was analysed using a Perkin-Elmer atomic absorption spectrometer AAnalyst 600 with graphite furnace (ETAAS – Electrothermal Atomic Absorption Spectrometry). The PerkinElmer AAnalyst 200 with flame atomization (FAAS – Flame Atomic Absorption Spectrometry) and PerkinElmer ELAN 6000DRC (ICP-MS Inductively Coupled Plasma Mass Spectrometry) were also used for determination of metalloid concentration in filtrates.
2.2.1 Influence of pH on metalloid sorption process

0.1 M NaOH and 0.1 M HCl were used for investigation of the pH impact. In glass vessels with 0.5 g of sorbent, the necessary amount of arsenic, antimony or tellurium stock solution was added. Then solutions of various pH were prepared by adding 0.1 M NaOH or 0.1 M HCl drop by drop to achieve pH values from 3 to 10. After that the reaction mixture was shaken for 24 h at the room temperature and filtered, and finally the pH scale was measured. The initial concentration of arsenic and tellurium used for the solution was 100 mg L\(^{-1}\) but the initial concentration of antimony was 200 mg L\(^{-1}\). Filtrates were analysed with FAAS or ETAAS.

2.2.2 Influence of competing ions on metalloid sorption process onto Fe-modified peat

KH\(_2\)PO\(_4\), Na\(_2\)NO\(_3\), NaCl, Na\(_2\)SO\(_4\), Na\(_2\)C\(_2\)O\(_4\), C\(_6\)H\(_4\)KNaO\(_6\) \(\times\) 7H\(_2\)O, Na\(_2\)CO\(_3\), Na\(_2\)SiO\(_3\), and also humic acid (peat derived from the Gagu Bog, Latvia) were used to investigate metalloid sorption in the presence of competing anions. In all cases, the anion concentration was 25 mg L\(^{-1}\), while the concentration of humic acid was 125 mg L\(^{-1}\). The initial arsenic concentration varied from 10 mg L\(^{-1}\) to 300 mg L\(^{-1}\), but concentrations of antimony and tellurium varied from 10 mg L\(^{-1}\) to 400 mg L\(^{-1}\). The sorption experiment was continued for 24 h at room temperature. Filtrates were measured using FAAS or ETAAS.

2.2.3 Sorption kinetics of metalloids onto Fe-modified peat

Sorption experiments were performed in the same manner as previously described. The initial As concentration was 100 mg L\(^{-1}\), while the initial concentration of Sb and Te was 200 mg L\(^{-1}\). In a 100 mL glass vessel with 0.5 g of a sorbent, 40 mL of metalloid solution was added. Vessels were shaken, and the metalloid content in the solution phase was measured after 0.2, 0.5, 0.7, 0.8, 1.0, 1.3, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 24.0 h, using ETAAS.

Experiments of sorption kinetics depending on the temperature were provided as previously mentioned, but the shaking was done at 275 K, 283 K, 298 K and 313 K temperature.

3 Results and discussion

3.1 Characterisation of sorbents

The content of organic substances as well as moisture content, Fe\(_2\)O\(_3\) analysis, nitrogen adsorption isotherm measurements, FT-IR spectra and SEM images were used to characterise the sorbents. Some characteristics of sorbents are given in Table 1. The content of organic matter for Fe-modified peat sorbents varied from 72% to 79% (Table 1). The content of organic matter was reduced in modified materials in comparison with unmodified materials. For example, organic matter in Fe-modified peat (Gagu) was 74%, but in raw peat material it was higher (99%). There were no significant changes observed in the content of C, H, N and O among all used materials.

The obtained results indicated that the applied method of modification was effective, because the content of Fe\(_2\)O\(_3\) was significantly enhanced after modification. For example, the peat layer (50–60 cm) from the Gagu Bog originally contained 4.1 mg g\(^{-1}\) of Fe\(_2\)O\(_3\) while the Fe\(_2\)O\(_3\) content reached 424.8 mg g\(^{-1}\) after modification.

Fe-modified peat had the highest content of Fe\(_2\)O\(_3\), and its specific surface area (obtained by the BET method) was one of the highest in comparison to other Fe-modified peat sorbents used in this study (Table 1). Specific surface area is one of the most important parameters that affect sorption and, taking into account the high affinity of metalloids to interact with iron compounds, one can predict that sorbents with the highest specific surface area and the highest content of iron oxide will also have the highest sorption capacity. In this case, modified peat (Gagu) has relevant properties that could ensure high sorption capacity and thus it could be effective for removal of metalloids.

The pH of the point of zero charge (pH\(_{\text{pzc}}\)) is one of the parameters that characterises the surface chemical properties of studied materials. The pH of the point of zero charge is understood as the pH above which the total surface of a sorbent is negatively charged while the surface at pH < pH\(_{\text{pzc}}\) has a positive charge [19]. The surface morphology of fused sorbents differs slightly (Fig. 1). Decomposed plant residues are characteristic to the raw peat material (Fig. 1a), and differences of surface morphology between raw and modified peat are obvious when comparing images a and b in Fig. 1. Plant residues coated with iron compounds are characteristic to modified peat.
FT-IR spectrometry is one of the methods that is used to characterise sorbent materials as it provides an opportunity to establish the main functional groups that are present in a sorbent as well as noticing differences in unmodified and modified materials.

Comparing the FT-IR spectra of Fe-modified and raw peat materials (Fig. 2), the main differences are observed at the wavenumber interval 1700–450 cm$^{-1}$, whereas common features for all the FT-IR spectra of investigated sorbent materials are as follows: a broad band at 3600–3300 cm$^{-1}$ which corresponds to hydroxyl groups in phenols and carboxylic acids and a band at 3570–3200 cm$^{-1}$ which corresponds to H valence vibrations in hydroxyl groups (Coates 2000). The signal detected at 2900 cm$^{-1}$ characterises methine group (>$\text{CH}$-) CH valence vibration, whereas the signal at 1430 cm$^{-1}$ characterises asymmetric/symmetric bends of the methyl group (C-H); and at interval 1225–950 cm$^{-1}$ aromatic C-H bend signal was observed [20]. The signal of FT-IR at 1700 cm$^{-1}$ characterises vibration of the carbonyl group that corresponds to carboxylic acids and esters (1700–1725 cm$^{-1}$), whereas characteristic vibrations of the aromatic ring are usually observed at interval 1615–1580 cm$^{-1}$. The signal at interval 1510–1450 cm$^{-1}$ also characterises vibrations of the aromatic ring (C=C-C bonds) [20].

The intensity of signals of several functional groups varies for modified and unmodified materials, thus indicating formation of Fe complexes and corresponding structural changes in molecules that have occurred due to interaction with metals. Normalization of FT-IR spectra was performed using the program Spectrum v 5.3.1 and the relation of band intensities at 1700 and 1600 cm$^{-1}$ were used to compare appropriate signals of functional groups before and after material modification. The obtained results are in agreement with previous studies discussed in the literature, for example, in the report by Rodriguez-Lucena et al. [21], it was noted that the bands at 2940, 2830, 1715, 1500, and 1050 cm$^{-1}$ are less intensive after formation of complexes with iron compounds. The lower intensity of separate bands may be related to formation of Fe phenolates and carboxylates. Such bands could be stretching of CH, C=O (carbonyl) and COOH, deformation if CH, vibrations of the aromatic ring, skeletal vibrations of aromatic C=C, and vibrations of C-O, C-C and C-OH [21].

Carboxylic, hydroxyl and amino groups probably could be the main functional groups that can interact with metalloids;

### Table 1: Characterisation of sorbents.

| Sorbent                 | LOI, % | Elemental content, % | Fe$_2$O$_3$, mg g$^{-1}$ | Specific surface area (after BET method), m$^2$ g$^{-1}$ | pH$_{zpc}$ |
|-------------------------|--------|----------------------|---------------------------|--------------------------------------------------------|-------------|
| mod. peat (Gagu)        | 72.6   | 0.5                  | 33.4                      | 4.7                                                    | 61.4        | 424.8 | 44.16 | 4.7 |
| mod. peat (Silu)        | 79.4   | 0.6                  | 32.1                      | 4.4                                                    | 62.9        | 259.7 | 43.79 | 4.6 |
| mod. peat (D. Veikenieks)| 73.5   | 0.1                  | 30.7                      | 4.5                                                    | 64.7        | 372.1 | –     | 6.6 |

**Figure 1:** SEM images of a) raw peat material, b) modified peat.
and this could explain sorption of metalloids on raw peat material, while the metalloid-O-Fe bond could support interaction between metalloids and Fe-modified peat.

Although the spectra of FT-IR give important data, they cannot give complete information regarding the results of modification; FTIR spectra provide indirect information to discuss the formation process of Fe complexes on the surface of sorbents.

### 3.2 Sorption efficiency

After the modification of peat with Fe compounds enhancement of the sorption capacity of the material was achieved. Three different types of peat were used for As(V) sorption. The sorbed amount of arsenic differs, but in all cases it was considerably higher for Fe-modified peat in comparison with raw peat material (Fig. 3).
The highest sorption capacity has Fe-modified peat (from the Gagu Bog) sorbing either As(V) as well as As(III), As(org.) and Sb(V) in comparison with Fe-modified peat sorbents where peat is obtained in the Silu Bog or the Dizais Veikenieks Bog (Fig. 4). However, Fe-modified peat from the Silu Bog can effectively remove Te(VI), but Fe-modified peat from the D. Veikenieks Bog could be the most effective sorbent for Sb(III) removal.

The obtained data indicated that sorption capacity depends on the material of used sorbent, even at similar reaction conditions. The highest sorption capacity of As(V) was observed for the Fe-modified peat (peat from the Gagu Bog) sorbent. The sorption capacity of Fe-modified peat (Gagu) reached 15.11 mg g⁻¹ (Fig. 4), i.e., this sorbent was capable of sorbing more than 90% of As(V) at the initial As(V) concentration of 179 mg L⁻¹; ability for sorption is reduced to 70% at the initial As(V) concentration of 269 mg L⁻¹. Reduction of sorption ability of the sorbent with increasing concentration of metalloid is affected by Fe/As ratio because increasing concentration of metalloid causes a reduction in the number of free sorption sites.

Fe-modified peat sorbents have considerably higher sorption ability for arsenites than arsenates. The highest sorption capacity was observed for Fe-modified peat (peat from the Gagu Bog) (44.8 mg g⁻¹). It was capable of removing more than 90% of As(III) at the initial As(III) concentration of 192 mg L⁻¹ but its sorption ability was reduced to 60% when the initial As(III) concentration reached 928 mg L⁻¹. Relatively high sorption capacity was observed for Fe-modified peat samples (peat from the Silu Bog and the D. Veikenieks Bog) – 25.8 mg g⁻¹ and 20.4 mg g⁻¹, respectively.

The studied types of sorbents were also able to remove the organic form of arsenic As(org.). The oxidation state of arsenic is +5. Sorption capacity of the sorbents was slightly lower sorbing As(org.) in contrast to As(V). The highest sorption ability applied to Fe-modified peat (Gagu) – its sorption capacity reached 11.45 mg g⁻¹. It was capable of sorbing more than 90% of As(org.) at the initial As(org.) concentration of 25 mg L⁻¹.

In comparison to arsenic (Fig. 4), removal of antimony(V) using Fe-modified peat is considerably more efficient (about two times higher). Sorption capacity of Fe-modified peat (Gagu) reached 40 mg g⁻¹ at the initial Sb(V) concentration of 730 mg L⁻¹. Fe-modified peat could sorb up to 95% of Sb(V) at the initial Sb(V) concentration of 370 mg L⁻¹, but less (only up to 75%) at the initial Sb concentration of 730 mg L⁻¹.

Fe-modified peat could effectively remove Sb(III), its sorption capacity reached 32 mg g⁻¹. Fe-modified peat could sorb up to 94% at the initial Sb(III) concentration of 365 mg L⁻¹, but the sorbed amount of Sb(III) decreased to 57% when the initial Sb(III) concentration reached 702 mg L⁻¹.

The results obtained for Fe-modified peat showed good sorption ability for Te(IV) (Fig. 4). Moreover, sorption capacity of Fe-modified peat (Gagu) reached 40 mg g⁻¹. Sorbents were capable of removing up to 90% of Te(IV) at the initial Te(IV) concentration of 380 mg L⁻¹.

In summary, sorbents synthesized in this study can be used for removal of metalloids (As, Sb, Te). Fe-modified peat (Gagu) was the most effective sorbent for all forms of metalloids. It is possible to use Fe-modified peat (Gagu) as a sorbent for severely polluted waters with extremely high concentrations of metalloids. Properties of the sorbent regarding the removal of metalloids might be related to the fact that peat is rich in organic substances each with their own diverse properties, but dominant functional groups are carboxyl groups and phenolic hydroxyls. Amino groups
have minor importance but also they might contribute to the sorption process of metalloids. It is characteristic that there are hydrophobic structures in peat organic matter possibly contributing to the sorption of arseno-organic species. Thus, based on literature studies and obtained FT-IR spectra, it can be suggested that iron is chemically bound, but the sorption is a joint effect of structural units of peat organic matter with iron oxo(hydroxides).

Sorption capacity of sorbents varies with sorption of different metalloids such as As(V), Sb(V) and Te(VI). This can be explained by specific chemical properties of each form of metalloid. Although arsenate and antimonate have similar chemical properties, their sorption still can be affected by molecular size and coordination. For example, arsenate is a tetrahedral oxoanion, but antimonate is an octahedral oxoanion, also molecules of antimonate have larger ionic radii and lower charge density.

The results of sorption experiments often are compared with theoretical sorption models such as Langmuir, Freundlich, Dubinin-Radushkevich, Redlich-Peterson model and others [22-25]. Obtained sorption isotherms for arsenic, antimony and tellurium were compared using Langmuir and Freundlich sorption isotherm models.

The Langmuir equation (Eq. 4) is used to characterise equilibrium between sorbed metal ions and metal ions in the solution. To determine the appropriate isotherm a linear form of the equation is often used. It is possible to linearize the Langmuir equation in four different types. However, the Langmuir equation (Eq. 5) is the most popular and the most appropriate for the assessment of experimental data.

\[ q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \]  

where \( C_e \) is the equilibrium concentration (mg L\(^{-1}\)); \( q_m \) is the amount of arsenic sorbed onto solid phase (mg g\(^{-1}\)); \( K_a \) are Langmuir constants which are related to sorption capacity and sorption energy, respectively, according to [26,27]. Moreover, \( q_m \) is \( q_e \) for a complete monolayer (mg g\(^{-1}\)) and \( K_a \) is the sorption equilibrium constant (L mg\(^{-1}\)) [27].

The Freundlich sorption isotherm model (Eq. 6) is one of the most often used models.

\[ q_e = K \left( \frac{C_e}{q_m} \right)^n \]  

where \( K \) and \( n \) are Freundlich constants which correspond to adsorption capacity and adsorption intensity, respectively. In the base of the Freundlich model there is an assumption that the sorption surface is heterogeneous and sorption sites have diverse energy. The obtained data can be linearized using linear Freundlich equation (Eq. 7).

\[ \log q_e = \frac{1}{n} \log C_e + \log K \]  

The obtained sorption data were compared using the Langmuir and Freundlich isotherm models. Based on the correlation coefficients, in most of the cases the sorption of metalloids using Fe-modified peat as sorbents fitted better to the Langmuir isotherm model, but values of the determination coefficient usually were close, thus confirming that experimentally obtained sorption data corresponds to both theoretical isotherm models. However, it is not possible to maintain that one of the models is predominant.

Sorbed species are not homogenous; therefore, it is possible that sorbents have more than one sorption centre. Optimization was performed according to the Eq. (3), where Langmuir isotherm model constants – \( q_m \), \( K_a \), and \( k \), \( k_a \) which correspond to sorption capacity of each sorption site and sorption energy were determined.

Sorption of Fe-modified biomaterials can be explained with the forming of the metalloid-O-Fe bond indicated by values of \( q_m \) and \( K_a \). Theoretically very high sorption capacity (q_{max}) is obtainable for Fe-modified peat (Gagu) sorbing As(III), though their sorption energy is negligible. Also the second sorption centre has important significance indicated by q_{m2} and k_a. It can be assumed that the second sorption centre is a matrix. For example, sorbed amount of Sb(V) is relatively high on raw peat material.

In overall, sorption on Fe-modified materials is provided by metalloid-O-Fe bond formation and possible sorption sites in a matrix.

### 3.3 Impact of pH on sorption of metalloids

The effect of pH is one of the most important factors that influence the sorption of metalloids. It may affect the chemical form of the metalloid in solution as well as surface properties of the sorbent. The interval of pH 3–9 was chosen to display conditions comparable with possible environmental conditions. Inorganic arsenate species is negatively charged at pH 3–9, whereas the arsenite species is neutral (H\(_3\)AsO\(_4\)). Stable species of As(V) and appropriate pH values are as follows: H\(_3\)AsO\(_4\) (pH 0–2), H\(_2\)AsO\(_4\)_\(^-\) (pH 2–7), HAsO\(_3\)_\(^2-\) (pH 7–12), and AsO\(_4\)_\(^3-\) (pH 12–14) [4,11].
The sorption capacity of Fe-modified peat sorbing As(V) and As(organ.) was maximal at acidic pH values and much lower at alkaline pH values (Fig. 5). Fe-modified peat was capable of sorbing more than 98% of As at the initial As concentration of 100 mg L\(^{-1}\) at the pH interval 3.2–6.4, but with the increase of pH to 8.14, the sorbed amount of As was reduced to 70%. Contrarily, As(III) could be effectively removed using Fe-modified peat in a wide pH interval. Fe-modified peat sorbed more than 95% of As(III) at pH interval 2.76–6.96 and the sorption ability reduced to 88% at pH 9.9 (initial As(III) concentration 100 mg L\(^{-1}\)).

However, a similar trend was observed also for sorption of other Fe-modified materials. The best sorption conditions were observed at pH interval 3–6.5 for As(V) when \(\text{H}_2\text{AsO}_4^-\) is the predominant form in the solution. It can be supposed that the sorption of As(V) onto Fe-modified materials mainly occurred depending on interactions between the ionic species of the respective element and the charged surface groups of the sorbent. pH has an impact on both, the form of the element in the solution and the ionization potential of active sorption sites. Moreover, other researchers suggest that it is possible that adsorption occurs by means of reaction between the positively charged surface groups -FeOH\(^+\) and the arsenate ions which leads to the formation of surface complexes [6,28].

The surface charge of the sorbent is one of the most important parameters that may characterise protonation and deprotonation, thus giving important information about the sorption mechanism. As mentioned above, the pH of the point of zero charge \(\text{pH}_{\text{pzc}}\) is one of the parameters that characterises the surface chemical properties of the studied materials. The \(\text{pH}_{\text{pzc}}\) is pH above which total surface of the sorbent is negatively charged while the surface has a positive charge at \(\text{pH} < \text{pH}_{\text{pzc}}\) [19].

As summarized in Table 1, the \(\text{pH}_{\text{pzc}}\) values of the studied sorbents varied from 4.7 to 6.6. If, for example, the \(\text{pH}_{\text{pzc}}\) of Fe-modified peat (Gagu) is 4.7, it means that the surface of the sorbent is positively charged if \(\text{pH} < 4.7\), but arsenate has a negative charge, and therefore the sorption capacity is maximal. At \(\text{pH} > 4.7\), the sorbent surface becomes negatively charged and interaction between the active sorption sites on the sorbent and the negatively charged \(\text{H}_2\text{AsO}_4^-\) and \(\text{HAsO}_4^{2-}\) ions decreases. Another reason for the decrease of the sorption capacity in alkaline solution can be a competition for sorption sites between arsenate and hydroxide ions.

\(\text{pH}_{\text{pzc}}\) is a valuable parameter, even if it does not always explain the pH impact on sorption capacity because natural materials are not homogeneous and different other factors such as particle size and predominant functional groups of sorbents may influence it.

As(III) in the studied pH interval is neutral, therefore an electrostatic interaction between As(III) and Fe-modified peat does not occur. Sorption is likely to be determined by sorbent properties and oxidation of As(III) to As(V) is possible. The obtained results are in agreement with similar studies [29].

For Sb(III), the corresponding species are \([\text{SbO}^+\text{] and [Sb(OH)]}^+\) at \(\text{pH} < 3\), \(\text{Sb(OH)}_3^-\) and \(\text{HSbO}_3^-\) at pH interval 3–10, and \([\text{SbO}_4^{2-}\) at \(\text{pH} > 10\) [30]. Whereas predominant form of Sb(V) at pH interval 2–11 is \(\text{Sb(OH)}_5^-\) (Van Vleek et al. 2011; Xi et al. 2011). The highest sorption capacity of the studied sorbents sorbing Sb(III) was at the pH interval 6–9 where the predominant form is neutral \(\text{Sb(III)}\). The obtained results are in agreement with other studies [29–31]. Interaction mechanisms between \(\text{Sb(III)}\) and Fe-modified sorbents can involve ligand exchange and negatively charged complex formation.

As in the case of arsenic, the best pH interval for removal of antimony(V) is pH 2–5.5 when \(\text{Sb(OH)}_5^-\) is the predominant form. The sorption capacity was decreasing at \(\text{pH} > 5.5\). The reason for decrease of sorption capacity in alkaline solution could be a charge repulsion between negatively charged surface groups of the sorbent and the negatively charged \(\text{Sb(V)}\) ions; additionally competition for sorption sites between antimonate and hydroxide ions is possible.

The impact of pH on both removal of Te(IV) (Fig. 6) and Te(VI) was not significant at the studied conditions. As previously suggested, \(\text{H}_2\text{TeO}_4^-\) is the main form of tellurium(VI) in aqueous environment at pH range 7.5–11, while \(\text{H}_6\text{TeO}_6^-\) is the predominant form at pH < 7.7. Fe-modified peat (Gagu) was capable of sorbing more than 95% of Te(VI) at the initial Te concentration of 100 mg L\(^{-1}\), at the entire studied pH interval.
Overall, sorption ability of Fe-modified peat sorbing As(V) and Sb was affected by pH of solution, but the impact of pH was weaker in a case of As(III) and Te. Electrostatic interaction could be the basis of As(V) and Sb(V) sorption on Fe-modified peat. Contrarily, ligand exchange and oxygen bond formation and interaction with Fe compounds could be the basis of As(III), Sb(III) and Te sorption on Fe-modified peat.

3.4 Influence of competing substances on sorption of metalloids

Since Fe-modified peat (Gagu) was assessed as the most effective sorbent for the removal of all forms of metalloids, there is a need to understand whether it has the potential of use for the treatment of natural waters. The impact of competing substances also have to be studied. For this reason, several salts (KH$_2$PO$_4$, NaNO$_3$, NaCl, Na$_2$SO$_4$, Na$_2$C$_2$O$_4$, C$_8$H$_6$KNaO$_6 \times 7$H$_2$O, Na$_2$CO$_3$, Na$_2$SiO$_3$) as well as humic acid (isolated from peat taken from the Gagu Bog, Latvia) were selected. The results indicated that sulphate, nitrate, chloride and tartrate anions have a minor influence on sorption of As(V) onto Fe-modified peat (Fig. 7). The obtained sorption capacity for Fe-modified peat was 15.11 mg g$^{-1}$, whereas in the presence of SO$_4^{2-}$ anions it was 13.67 mg g$^{-1}$, and in the presence of NO$_3^-$, Cl$^-$ and tartrate anions – 13.12 mg g$^{-1}$, 15.01 mg g$^{-1}$ and 13.3 mg g$^{-1}$ respectively. The results of this study are in agreement with the research done under the supervision of Y. Zhang [36], who suggested that Cl$^-$, NO$_3^-$ and SO$_4^{2-}$ do not interfere with the removal of As(V) using Ce-Fe adsorbent.

In contrast to that, the presence of oxalate, phosphate and humic acid significantly reduced the removal rate of arsenic (Fig. 7). The sorption capacity decreased to 11.04 mg g$^{-1}$ in the presence of oxalate and phosphate ions, but even more significant reduction of sorption capacity was observed in the presence of humic acid. Sorption capacity was 10.13 mg g$^{-1}$ in the presence of PO$_4^{3-}$ anions, and this reduction indicates the competition between arsenate and phosphate for binding sites of the sorbent.

The reason for similar sorption behaviour of arsenate and phosphate on Fe-modified peat could be related to the fact that both acids (arsenate acid and phosphoric acid) are triprotic acids with similar structure and thus also with similar properties.

Sorption capacity of Fe-modified peat was 5.50 mg g$^{-1}$ in the presence of humic acid; consequently, humic acid may compete with arsenate for sorption sites of the sorbent. Therefore, Fe-modified peat used as a sorbent is less effective in waters containing high concentrations of humic acid. As reported in other studies, humic acids may be one of the main reasons that explain the decrease of sorption capacity in experiments in natural environments in comparison with laboratory experiments, e.g., it was confirmed by studies where tap water and groundwater in Mongolia was used [36]. However, further experiments are needed, e.g., in the areas of sorbent optimisation or development of new sorbents that could adsorb not only arsenic but also humic acid with the aim to prevent negative impact of humic acid on the sorption process, [37].

As it was observed in the sorption experiment with As(V), removal of Sb(V) is also slightly reduced in the presence of tartrate, carbonate and silicate, while the sorbed amount of Sb(V) was considerably decreased in the presence of oxalate and phosphate ions (Fig. 8). In contrast to As(V), the sorbed amount of Sb(V) on Fe-modified peat is enhanced in the presence of humic acid. Such results can be explained by Sb-HA complex formation. Moreover, sorption of Sb on HA that is attached to Fe-modified peat is possible.
The sorbed amount of Sb(III) on Fe-modified peat did not reduce in the presence of competing substances. The sorbed amount of Sb(III) is enhanced by 2–9% in the presence of oxalate, carbonate, sulphate, phosphate and humic substances. It is suggested that Sb(III) could be oxidized to Sb(V) in the presence of HA and also in the presence of Fe and Mn oxo(hydroxides) that promote oxidation process [35,38].

The sorbed amount of Sb(III) on Fe-modified peat did not reduce in the presence of competing substances. The sorbed amount of Sb(III) is enhanced by 2–9% in the presence of oxalate, carbonate, sulphate, phosphate and humic substances. It is suggested that Sb(III) could be oxidized to Sb(V) in the presence of HA and also in the presence of Fe and Mn oxo(hydroxides) that promote oxidation process [35,38].

The sorbed amount of Te(IV) did not reduce in the presence of nitrate and sulphate, but it slightly reduced in the presence of chloride, phosphate and carbonate. Fe-modified peat can remove 99% of Te(IV) at the initial Te(IV) concentration of 382 mg L⁻¹, but removal of Te(IV) was reduced to 98%, 81% and 80% in the presence of chloride (25 mg L⁻¹), phosphate (25 mg L⁻¹) and carbonate (25 mg L⁻¹), respectively. The sorbed amount of Te(IV) reduced to 72% in the presence of tartrate (25 mg L⁻¹), silicate (25 mg L⁻¹) and oxalate (25 mg L⁻¹). The sorbed amount of Te(IV) is substantially affected by the presence of HA when the sorbed amount of Te(IV) is only 17%.

Results can be interpreted by competition between Te ions and HA for sorption sites.

Fe-modified peat can sorb 55% of Te(VI) at an initial Te(VI) concentration of 390 mg L⁻¹. However, the sorbed amount of Te(VI) on Fe-modified peat reduced in the presence of carbonate (49%), sulphate (50%) and silicate (45%), and more obviously in the presence of tartrate (41%), oxalate (39%) and phosphate (36%).

Overall, the presence of competing ions as well as HA, affects sorption of metalloids on Fe-modified peat. A minor impact on the reduction of metalloid sorption was observed in the presence of nitrate, sulphate, carbonate and tartrate, while in the presence of phosphate and HA the sorption ability of metalloids can be considerably reduced. It is worth mentioning that the presence of HA negatively affects sorption of As(V) and Te(IV), whereas Fe-modified peat is not suitable for water purification with high content of HA, but it may effectively remove both, Sb(III) and Sb(V).

### 3.5 Sorption kinetics study of metalloids

Sorption kinetics gives valuable insight into the pathway of the sorption process and sorption mechanism. The sorption kinetics of metalloids on Fe-modified peat (Gagu) was studied as a function of time at room temperature. According to the results of the sorption kinetics study, the sorbed amount of each metalloid exceeded 55% after 1 h (Fig. 9). The sorbed amount of As(III) exceeded 90% after 2 h, while the sorbed amount of As(V) exceeded 90% after 15 h. More than 90% of Sb(III) and Te(IV) were removed after 1 h, but 90% of Sb(V) was removed in 2 h using Fe-modified peat.

In comparison with other studies it was determined that a contact time of 48 h is needed to reach the equilibrium using waste metal hydroxide entrapped in the beads of calcium alginate used as a sorbent; 1 h is needed for ferrihydrite; 4 h are needed to reach the equilibrium of As(V) sorption process using goethite and amorphous iron oxide; longer periods are necessary if Fe(III) (oxo)hydroxide-loaded cellulose beads and Fe(III)-loaded lignocellulosic substrates are used, 10 h and 24 h, respectively [16]. Sorption experiments of Sb(III) and Sb(V) onto Fe oxides (e.g., goethite) and clays (e.g., bentonite) indicated that the sorption process is fast. It is suggested that 24 h is sufficient time to reach sorption equilibrium of Sb(III) and a similar tendency is characteristic also for Sb(V) [32,39].

Several models are used to describe the model of the sorption kinetics process. In order to establish the
sorption model, sorption constants were calculated using the pseudo-first and pseudo-second-order equations. An appropriate sorption model was determined comparing the determination coefficients in the pseudo-first and pseudo-second-order equations. In all occasions experimental data fitted best to the pseudo-second-order kinetic model. The pseudo-second-order kinetic model was based on the assumption that chemisorption can be the rate-limiting step involving sharing valency forces or exchange of electrons between sorbent and sorbate [40].

The rate of the pseudo-second-order reaction may be dependent on the amount of sorbate sorbed and the amount sorbed at the equilibrium time. The integrated rate law for the pseudo-second-order reaction is shown in Eq. (8) [27].

\[
q_t = \frac{t}{(1/kq_e^2) + (t/q_e)}
\]  

where \(k\) is the rate constant of sorption \((\text{mg g}^{-1} \text{min}^{-1})\), \(q_e\) – the amount of metalloid sorbed onto Fe-modified peat at the equilibrium \((\text{mg g}^{-1})\), \(q_t\) – the amount of metalloid sorbed on the surface of Fe-modified peat at any time \(t\) \((\text{mg g}^{-1})\).

The linear form of Eq. (8) is:

\[
\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e}
\]  

Eq. (9) can be transformed to obtain Eq. (10):

\[
\frac{q_t}{t} = \frac{h}{1 + kq_te}
\]  

where \(h = kq_e^2\), and \(h\) characterises the initial sorption rate as \(q_t/t\), when \(t\to0\) [11]. Therefore, the plot of \(t/q_t\) against \(t\) reveals a linear relationship with the slope of \(1/q_e\) and intercept of \(1/kq_e^2\). The kinetic parameters of the sorption are given in Table 2.

Kinetic experiments depending on the temperature indicate that the sorbed amount of metalloid is increasing with increases of temperature. Such a trend is observed for each form of the studied metalloids. Experimentally obtained data corresponds to the pseudo-second-order kinetic model (determination coefficient is not lower than 0.996). Arrhenius equation shows the pseudo-second-order rate constant depending on the temperature (Eq. 11). It is possible to determine sorption activation energy using the Arrhenius equation. Activation energy is defined as an energy that must be overcome in order for a chemical reaction to occur. It also can be defined as an energy that must be overcome by the sorbate ion or molecule to interact with functional groups on the surface of the sorbent [41].

\[
k_2 = k_0 \cdot e^{-\frac{E_a}{RT}}
\]  

where \(k_2\) – rate constant of the pseudo-second-order equation \((\text{g mg}^{-1} \text{min}^{-1})\), \(k_0\) – temperature independent factor \((\text{g mg}^{-1} \text{min}^{-1})\), \(E_a\) – activation energy \((\text{kJ mol}^{-1})\), \(T\) temperature \((\text{K})\) and \(R\) is the ideal gas constant \((8.314 \text{ J mol}^{-1} \text{K}^{-1})\).

It is possible to show activation energy graphically. The plot of \(\ln k_2\) against \(1/T\) reveals a linear relationship with the slope of \(-E_a/R\) and intercept of \(\ln k_0\).

The calculated amount of activation energy for Fe-modified peat sorbing metalloids is given in Table 3.

Table 2: Calculated kinetic parameters of Fe-modified peat sorbing metalloids \((k – rate constant of sorption, h – the initial sorption rate)\).

| Metalloid | Sorbed, mg g^{-1} | k, g mg^{-1} min^{-1} | h, mg g^{-1} min^{-1} |
|-----------|------------------|-----------------------|------------------------|
| As(III)   | 7.64             | 0.0130                | 0.7606                 |
| As(V)     | 7.94             | 0.00171               | 0.1081                 |
| Sb(III)   | 14.33            | 0.0153                | 3.3387                 |
| Sb(V)     | 14.84            | 0.0014                | 0.2504                 |
| Te(IV)    | 7.51             | 0.02584               | 1.4583                 |
| Te(VI)    | 6.59             | 0.00214               | 0.0931                 |

Table 3: Calculated activation energy for Fe-modified peat sorbing metalloids.

| Metalloid | \(E_a\), kJ mol^{-1} |
|-----------|---------------------|
| As(III)   | 16.96               |
| As(V)     | 8.06                |
| Sb(III)   | 8.32                |
| Sb(V)     | 31.99               |
| Te(IV)    | 10.79               |
| Te(VI)    | 7.59                |
Mechanisms of physical sorption processes. Since activation energy of As, Te and Sb(III) is lower than 25 kJ mol^{-1} and the rate (limiting step of the sorption process) could be controlled by diffusion.

Competing ions as well as HA affect sorption of metalloids on Fe-modified peat. A minor impact on the reduction of metalloid sorption was detected in the presence of nitrate, sulphate, carbonate and tartrate ions, while in the presence of phosphate and HA sorption ability of metalloids can be considerably reduced. The sorption capacity of Fe-modified peat sorbing As(V), Sb(V) and Te(VI) reduced most significantly in the presence of phosphate and oxalate ions, while the sorbed amount of Te(VI) reduced also in the presence of tartrate ions. The presence of HA can negatively affect sorption of As(V) and Te(IV), whereas Fe-modified peat is not suitable for purification of water with high HA content, but it may effectively remove both, Sb(III) and Sb(V). Sorption of metalloids on Fe-modified peat mainly occurs relying on mechanisms of physical sorption processes.

Acknowledgements: This work was supported by the Latvia National Research program „ResProd”

References

[1] Ansari R., Sadegh M., Application of activated carbon for removal of arsenic ions from aqueous solutions, E-J. Chem., 2007, 4, 103-108.
[2] Ceriotti G., Amarasiiriwardena D., A study of antimony complexed to soil-derived humic acids and inorganic antimony species along a Massachusetts highway, Microchem. J., 2009, 91, 85–93.
[3] Filella M., Belzile N., Chen Y., Antimony in the environment: a review focused on natural waters I. Occurrence, Earth-Sci. Rev., 2002, 57, 125-176.
[4] Nemade P.D., Kadam A.M., Shankar H.S., Adsorption of arsenic from aqueous solution on naturally available red soil, J. Environ. Biol., 2009, 30(4), 499–504.
[5] Zhang L., Zhang M., Guo X., Liu X., Kang P., Chen X., Sorption characteristics and separation of tellurium ions from aqueous solutions using nano-TiO_{2}, Talanta., 2010, 83, 344–50.
[6] Dupont L., Jolly G., Aplincourt M., Arsenic adsorption on lignocellulosic substrate loaded with ferric ion, Environ. Chem. Lett., 2007, 5, 125–129.
[7] Negrea A., Clopec M., Davidescu C.M., Lupa L., Negrea P., Popa A., Adsorption Characteristic of As(V) onto Fe-XAD7-DEHPA Resin, Chemical Bulletin of “Politehnica” University of Timisoara, Romania., 2011, 56(70), 1–4.
[8] Zhang F.-S., Itoh, H. Iron oxide-loaded slag for arsenic removal from aqueous system, Chemosphere, 2005, 60, 319–25.
[9] Henke K. R. (Ed.) Arsenic: Environmental Chemistry, Health Threats, and Waste Treatment, Wiley, Wiltshire, 2009.
[10] Anirudhan T.S., Unnithan M.R., Arsenic(V) removal from aqueous solutions using an anion exchanger derived from coconut coir pith and its recovery, Chemosphere, 2007, 66, 60–66.
[11] Mohan D., Pittman C.U., Arsenic removal from water/ wastewater using adsorbents-A critical review, J. Haz. Mat., 2007, 142, 1–53.
[12] Pokhrel D., Viraraghavan T., Arsenic removal from an aqueous solution by a modified fungal biomass, Wat. Res., 2006, 40, 549–52.
[13] Steely S., Amarasiiriwardena D., Xing B., An investigation of inorganic antimony species and antimony associated with soil humic acid molar mass fractions in contaminated soils, Environ. Pollut., 2007, 148, 590–598.
[14] Harada T., Takahashi Y., Origin of the difference in the distribution behavior of tellurium and selenium in a soil–water system, Geochim. Cosmochim. Acta., 2008, 72, 1281–1294.
[15] Narukawa T., Separation and determination of tellurium(IV) and -VI by electrothermal atomic absorption spectrometry using a tungsten furnace after collection as the 3-phenyl-5-mercapto-1,3,4-thiadiazole-2(3H)-thione–tellurium complex on cobalt(III) oxide, J. Anal. Atomic Spectrom., 1999, 14, 75–80.
[16] Escudero C., Fiol N., Villaescusa I., Bollinger J.-C., Arsenic removal by a waste metal (hyd)oxide entrapped into calcium alginate beads., J. Haz. Mat., 2009, 164, 53–61.
[17] Heiri O., Lotter A.F., Lemcke, G. Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results, J. Paleolimnol., 2001, 25, 101–110.
[18] Fiol N., Villaescusa I., Determination of sorbent point zero charge: usefulness in sorption studies, Environ. Chem. Lett., 2009, 7, 79–84.
[19] Aldegs Y., Elbarghouthi M., Elsheikh A., Walker G., Effect of solution pH, ionic strength, and temperature on adsorption behavior of reactive dyes on activated carbon, Dyes Pigments., 2008, 77, 16–23.
[20] Coates J., Interpretation of Infrared Spectra, a practical approach, In: Encyclopedia of Analytical Chemistry Ed. Meyers R.A. Chichester: John Wiley and Sons Ltd., 2000, 10815–10837.
[21] Rodríguez-Lucena L., Lucena P., Hernández-Apaolaza J. I., Relationship between the structure of Fe-Lignosulfonate complexes determined by FTIR spectroscopy and their reduction by the leaf Fe reductase, In The proceedings of the international plant nutrition colloquium XVI UC Davis. August 26–30, 1–4. Sacramento, California. University of California, 2009.
[22] Ho Y.-S., Review of second-order models for adsorption systems., J. Haz. Mat., 2006, 136, 681–689.
[23] Febrianto J., Kosalish A.N., Sunarso J., Ju Y.-H., Indraswati N., Ismadji S., Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: a summary of recent studies., J. Haz. Mat., 2009, 162, 616–45.
[24] Smedley P.L., Kinniburgh D.G., A review of the source , behaviour and distribution of arsenic in natural waters, Appl. Geochem., 2002, 17, 517–568.
[25] Kinniburgh D.G., General Purpose Adsorption Isotherms, Environ. Sci. Technol., 1986, 20, 895–904.
Sorption of V and VI group metalloids (As, Sb, Te) on modified peat sorbents

[26] Kuriakose S., Singh T.S., Pant K.K., Adsorption of As(III) from Aqueous Solution onto Iron Oxide Impregnated Activated Alumina, Wat. Qual. Res. J. Canada., 2004, 39(3), 258–266.

[27] Ho Y.-S., Ofomaja A.E., Kinetics and thermodynamics of lead ion sorption on palm kernel fibre from aqueous solution, Process Biochem., 2005, 40, 3455–3461.

[28] Payne K., Abdel-Fattah T., Adsorption of Arsenate and Arsenite by Iron-Treated Activated Carbon and Zeolites: Effects of pH, Temperature, and Ionic Strength, J. Environ. Sci. Health, Pt A., 2005, 40, 723–749.

[29] Partey F., Norman D., Ndur S., Nartey R., Arsenic sorption onto laterite iron concretions: temperature effect., J. Colloid Interface Sci., 2008, 321, 493–500.

[30] Uluozlu O.D., Sarı A., Tuzen M., Biosorption of antimony from aqueous solution by lichen (Physcia tribacia) biomass, Chem. Eng. J., 2010, 163, 382–388.

[31] Van Vleek B., Amarasiriwardena D., Xing B., Investigation of distribution of soil antimony using sequential extraction and antimony complexed to soil-derived humic acids molar mass fractions extracted from various depths in a shooting range soil, Microchem J., 2011, 97, 68–73.

[32] Xi J., He M., Lin C., Adsorption of antimony(III) and antimony(V) on bentonite: Kinetics, thermodynamics and anion competition, Microchem. J., 2011, 97, 85–91.

[33] Sarı A., Uluozlü Ö.D., Tüzen M., Equilibrium, thermodynamic and kinetic investigations on biosorption of arsenic from aqueous solution by algae (Maugeotia genuflexa) biomass, Chem. Eng. J., 2011, 167, 155–161.

[34] Biswas B.K., Inoue J., Kawakita H., Ohto K., Inoue K., Effective removal and recovery of antimony using metal-loaded saponified orange waste., J. Haz. Mat., 2009, 72, 721–728.

[35] Buschmann J., Sigg L., Antimony (III) Binding to Humic Substances: Influence of pH and Type of Humic Acid, Environ. Sci. Technol., 2004, 38, 4535–4541.

[36] Zhang Y., Yang M., Huang X., Arsenic(V) removal with a Ce(IV)-doped iron oxide adsorbent., Chemosphere, 2003, 51, 945–952.

[37] Giasuddin A.B.M., Kanel S.R., Choi H., Adsorption of Humic Acid onto Nanoscale Zerovalent Iron and Its Effect on Arsenic Removal, Environ. Sci. Technol., 2007, 41, 2022–2027.

[38] Sh T., Liu C.-Q., Wang L., Antimony coordination to humic acid: Nuclear magnetic resonance and X-ray absorption fine structure spectroscopy study, Microchem. J., 2012, 103, 68–73.

[39] Xi J., He M., Wang K., Zhang G., Adsorption of antimony(III) on goethite in the presence of competitive anions, J. Geochem. Explor., 2013, 132, 201–208.

[40] Ho Y.S., Mckay G., The kinetics of sorption of divalent metal ions onto sphagnum moss peat, Water Res., 2000, 34(3), 735-742.

[41] Saha P., Chowdhury S., Insight into adsorption thermodynamics, 2011, http:/cdn.intechopen.com/pdfs/13254.pdf

[42] T.S. Anirudhan, P.S. Suchithra, Equilibrium, kinetic and thermodynamic modeling for the adsorption of heavy metals onto chemically modified hydrotalcite, Indian J. Chem. Technol., 2010, 17, 247–259.

[43] Ayoob S., Gupta A. K., Bhakat P.B., Bhat V.T., Investigations on the kinetics and mechanisms of sorptive removal of fluoride from water using alumina cement granules, Chem. Eng. J., 2008, 140, 6–14.

[44] Bekçi Z., Seki Y., Cavas L., Removal of malachite green by using an invasive marine alga Caulerpa racemosa var. cylindracea., J. Haz. Mat., 2009, 161, 1454–1460.

[45] Chen A.-H., Chen S.-M., Biosorption of azo dyes from aqueous solution by glutaraldehyde-crosslinked chitosans., J. Haz. Mat., 2009, 172, 1111–21.

[46] Suteu D., Malutan T., Industrial Cellolignin Wastes as Adsorbent for Removal of Methylene Blue Dye from Aqueous Solutions, BioResources, 2013, 8(1), 427–446.