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FACULTY OF GEOGRAPHY AND EARTH SCIENCES
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SORPTION OF V AND VI GROUP METALLOIDS ON MODIFIED BIOMATERIAL SORBENTS

Summary of Doctoral Thesis

Submitted for the degree of Doctor of Chemistry in Environmental Science
Subfield of Environmental Chemistry and Ecotoxicology

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The thesis contains the introduction, 3 chapters, conclusions and reference list.
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CONTENTS

Introduction

Recently, growing attention is being paid to environmental pollution with metalloids (As, Sb, Te) (Ansari and Sadegh 2007, Ceriotti and Amarasiriwardena 2009, Filella *et al.* 2002, Nemade *et al.* 2009, Zhang *et al.* 2010). 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 well known toxic element that can be found in drinking water at problem affected areas, for example, in SE Asia. Concentration of arsenic in these areas exceeds maximal permissible levels several times (Dupont *et al.* 2007, Negrea *et al.* 2011, Nemade *et al.* 2009, Zhang and Itoh 2005). Arsenic can enter into natural water systems through the 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 (Anirudhan and Unnithan 2007, Henke 2009, Mohan and Pittman 2007).

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 (Ansari and Sadegh 2007, Pokhrel and Viraraghavan 2006). In media with pH 3–9, the dominant species of As(III) is neutral H_3AsO_3, while those of As(V) are negatively charged $HAsO_4^{2-}$ and $H_2AsO_4^{-}$ (Nemade *et al.* 2009).

Antimony, like arsenic, is 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, while in polluted areas – close to anthropogenic sources – concentration can be up to 100 times higher in comparison with natural levels (Filella *et al.* 2002).

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), also Sb(V) is the predominant species in oxic systems and Sb(III) in anoxic systems; although some studies reveal that significant amount of Sb(III) can be also found in oxic and Sb(V) in anoxic systems (Filella *et al*. 2002, Steely *et al*. 2007).

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 (Zhang *et al.* 2010). Aqueous Te species mainly exist in the form of oxyanions – tellurite (TeO_3^{2-}) and tellurate (TeO_4^{2-}) or hydroxide anions ($Te(OH)_6$, $TeO(OH)_3^{-}$). Te(VI) is the predominant form in aqueous media under oxic conditions, whereas Te(IV) predominates under reducing conditions (Harada and Takahashi 2009, Narukawa 1999).

Although many different sorbents have been used for metal and metalloid removal from water and soil so far, and due to unsatisfactory efficiency and high costs of these sorbents, opportunities are still open for finding new environmentally friendly and cost effective sorbents. Recently, great attention has been paid to the investigation of sorbents based on natural materials. Some studies have demonstrated that inorganic forms of arsenic, antimony as well as tellurium can strongly bind to Fe-containing compounds (Hein *et al*. 2003, Leuz *et al*. 2006, Rakshit *et al*. 2011).

Topicality of thesis

Different refinement technologies are used to reduce pollution of metalloids, for example, precipitation, sorption, ion exchange, extraction and cementation. Each of them 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 (Anirudhan and Unnithan 2007, Dupont *et al.* 2007, Negrea *et al*. 2011, Zhang and Itoh 2005).

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 (Escudero *et al*. 2009).

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

Aim of the thesis

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

Tasks of the thesis

- To perform the synthesis of biomaterial based sorbents and to characterize them;
- To investigate sorption of metalloids – arsenic, antimony and tellurium - on iron modified biomaterial sorbents;
- To investigate sorption of metalloids on iron modified biomaterial sorbents depending on the different physicochemical parameters such as element form and concentration of a metalloid, pH, ionic strength, competing anions, temperature and time;
- To determine sorption model of V and VI group metalloids onto modified biomaterial sorbents.

Proposed theses

- Modification of materials with Fe compounds significantly enhance the sorption capacity of investigated sorbents used for sorption of metalloids.
- Fe-modified materials can be effectively used for removal of metalloids.
- Sorbed amount of metalloids onto sorbents is affected by pH of a solution, ionic strength, temperature, as well as presence of competing ions and humic substances.
- Assessment of physical-chemical parameters on metalloid sorption onto Fe-modified materials provides useful information about the mechanism of sorption process as well as indicates practical applications of sorbents.

Scientific novelty

New knowledge about interaction character of V and VI group metalloids with biomaterials are obtained as a result of thesis. Acquired knowledge may be useful to understand element behaviour in the environment as well as investigation of which methods and materials are possible to use for environment refinement in case of pollution with studied metalloids was done. For instance, investigation of V and VI group metalloid sorption on sorbents of natural origin can provide new knowledge for optimization of existing sorbents as well as for development of new sorbents.

Remediation of polluted environment using sorbents made on iron modified peat is innovative solution because until now there are no data reported about metalloid sorption on such peat sorbents.

Potential practical applications

In the PhD thesis the development of high value-added sorbent has been performed using peat, one of the most significant mineral resources in Latvia. Moreover, potential use of application of peat has been investigated. Potential applications of peat as a sorbent and modification method of peat have been evaluated as well as the impact of different parameter impact on sorption capacity has been investigated.

Approbation

The results of the doctoral thesis are published in 11 scientific articles, presented in 15 reports at international conferences and in 7 reports at local conferences in Latvia.

Scientific publications:

1. Ansone L., Eglīte L., Kļaviņš M. (2011) Kūdras sorbenti arsēna savienojumu adsorbcijai. [In Latvian] *Materiālzinātne un lietišķā ķīmija*[1], 24 (1), 95–99.
2. Klavins M., Porshnov D., Ansone L., Robalds A., Dreijalte L. (2012) Peat as natural and industrial sorbent. In: Ramos, R. A. R., Straupe, I., Panagopoulos, T. (eds.) *Recent Researches in Environment, Energy Systems & Sustainability, WSEAS Press*[2], 146–151.
3. Ansone L., Eglite L., Klavins M. (2012) Removal of arsenic compounds with peat, peat-based and synthetic sorbents. *Journal of Ecological Chemistry and Engineering S*[3], 19(4), 513–531.
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5. Ansone L., Klavins M., Viksna A. (2013) Arsenic removal using natural biomaterial-based sorbents. *Environmental Geochemistry and Health*[5], 35 (5), 633–642. DOI 10.1007/s10653-013-9546-7
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9. Jankēvica M., Ansone L., Kļaviņš M. (2013) Antimona (V) sorbcijas izpēte uz modificētiem biomateriālu sorbentiem. [In Latvian] *Materiālzinātne un lietišķā ķīmija*[1], 29, 101- 107.
10. Ansone L., Klavins M., Jankevica M., Viksna A. (2014) Biomass sorbents for metalloid removal. *Adsorption*[7], 20 (2), 275–286.
11. Ansone-Bertina L., Klavins M., Jankevica M. Biomaterial Sorbents for Antimony and Tellurium Removal. *Submitted: Environmental Geochemistry and Health.*

Patents:

1. Kļaviņš M., Ansone L**.** (2011) Sorbenta sintēzes metode dzeramā ūdens attīrīšanai no arsēna savienojumiem. [In Latvian] LV 14398 B, 20.10.2011.
2. Robalds A., Dreijalte L., Ansone L., Kļaviņš M. (2012) Sorbents ūdeņu attīrīšanai no fosfora savienojumiem. Latvijas patents uz izgudrojumu [In Latvian] LV 14518 B, 20.07.2012.

Reports presented at the international conferences:

1. Ansone L., Eglite L., Klavins M., Purmalis O. Peat sorbents for sorption of arsenic compounds. In: 9th International Conference “Humic Substances in Ecosystems 9”, Karpacz, Karkonosze Mts.,

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[1] Indexed in: EBSCO, CSA/ProQuest, VINITI, Chemical Abstracts.

[2] Indexed in: Scopus – Conference Proceedings.

[3] Indexed in: Web of Science, Elsevier – SCOPUS**.**

[4] Indexed in: Chemical Abstracts Service (CAS), EBSCO Discovery Service.

[5] Indexed in: Web of Science, SCOPUS.

[6] Indexed in: Web of Science, SCOPUS.

[7] Indexed in: Web of Science, SCOPUS.

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10. Klavins M., Ansone L., Robalds A., (2013) Peat as sorbent in nature and industry. In: Abstracts of 14th EuCheMS International conference on chemistry and the Environment. Barcelona, Spain, PS7
11. Ansone L., Jankevica M., Klavins M. (2013) Peat sorbents for metalloid – arsenic, antimony and tellurium removal. In: „Peat and humic substances and their application" Latvia, Riga, October 10–12.
12. Jankevica M., Ansone L., Klavins M. Arsenic, Antimony and Tellurium Removal using Fe-modified Biomaterials. In: 18th International Scientific Conference „EcoBalt" 2013, Vilnius, Lithuania, October 25–27. Book of abstracts, 53.
13. Ansone-Bertina L., Klavins M., Jankevica M. (2014) Biomaterial Sorbents for Antimony and Tellurium Removal In: Proceedings of the 4th International Conference on Environmental Pollution and Remediation (ICEPR 14). August 11–13, Prague, Czech Republic.
14. Ansone-Bertina L., Jankevica M., Klavins M., Actins A. (2014) Metalloid removal using Fe-modified biomaterials. In: Book of Abstracts of the 19th International scientific conference „EcoBalt 2014". October 8–10, Riga, Latvia.
15. Ansone-Bertina L. (2014) Fe-Modified Biomaterials for Metalloid Removal. In: Book of Abstracts of the 9th International Conference on Establishment of Cooperation between Companies and Institutions in the Nordic Countries, the Baltic Sea Region, and the World „Linnaeus Eco-TECH 2014". November 24–26, Kalmar, Sweden.

Reports presented at local conferences in Latvia:

1. Ansone L., Eglīte L., Kļaviņš M. Kūdras sorbenti arsēna savienojumu sorbcijai. LU 69. konference, Rīga, Latvija, februāris – maijs, 2011. Latvijas Universitātes 69. Zinātniskā konference Ģeogrāfija, Ģeoloģija, Vides zinātne Referātu tēzes, 406–407.

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3. Ansone L., Kļaviņš M., Jankēvica M. Biosorbentu izmantošana metaloīdu sorbcijai. LU 71. konference, Rīga, Latvija, februāris – maijs, 2013. Latvijas Universitātes 71. Zinātniskā konference Ģeogrāfija, Ģeoloģija, Vides zinātne Referātu tēzes, 406–408.
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5. Kļaviņš M., Ansone L., Robalds A., Poršņovs D. Kūdra kā sorbents dabā un tehnoloģijās. LU 72. konference, Rīga, Latvija, februāris – maijs, 2014. Latvijas Universitātes 72. Zinātniskā konference Ģeogrāfija, Ģeoloģija, Vides zinātne Referātu tēzes, 314–315.
6. Jankēvica, M., Ansone, L., Kļaviņš, M. Antimona (V) sorbcijas izpēte uz modificētiem biomateriālu sorbentiem. LU 72. konference, Rīga, Latvija, februāris – maijs, 2014. Analītiskās un fizikālās ķīmijas sekcija.
7. Ansone-Bērtiņa L., Kļaviņš M., Vīksna A., Actiņš A. V un VI grupas metaloīdu sorbcijas izpēte uz modificētiem biomateriālu sorbentiem. Latvijas Universitātes 73. Zinātniskā konference Zemes un vides zinātņu sekcijas referātu un stenda referātu sesija „Purvu bioloģiskā daudzveidība, izpēte un resursu racionāla izmantošana" Rīga, Latvija, februāris – maijs, 2015.

1. Literature review

1.1. Sources and content of metalloids in the environment

There are different routes how metalloids can enter the environment. It is possible through the range of natural and anthropogenic sources. Arsenic is a naturally occurring element that ranks on the 47th place among 88 naturally occurring elements. Moreover, elemental arsenic as well as oxide and sulphide forms of arsenic are found in the structure of more than 245 minerals (Rawat 2000, Shipley 2007, Vaughan 2006). Since prehistoric times, arsenic constantly has been in the centre of attention.

Arsenic enters natural water systems through the range of anthropogenic as well as natural sources. For example, mobilisation of natural arsenic-bearing deposits, biological activity and volcanic emissions as well as soil erosion and leaching are some natural sources of arsenic. Anthropogenic sources of arsenic include discharges from various industries such as smelting, petroleum refinery, glass manufacturing, fertiliser production and intensive application of insecticides and herbicides containing arsenic (Anirudhan and Unnithan 2007, Henke 2009). Natural weathering processes release approximately 40,000 tonnes of arsenic into the environment annually, while the amount released by human activities is two times higher (Thirunavukkarasu *et al.* 2001).

The concentration of arsenic in uncontaminated stream waters ranges from 0.1 to 1.7 μg/L, but in ground waters from 0.1 to 7500 μg/L worldwide. Arsenic content in uncontaminated soil varies from 0.2 to 40 mg/kg, but the levels can reach 100–2500 mg/kg in the vicinity of copper smelters. Moreover, in soil of orchards where arsenical pesticides were used in the past, the content of arsenic may range from 200 to 2500 mg/kg (Chen 2011). Arsenic is present also in the atmosphere. Volcanic activity is the main natural source of arsenic and only minor proportions are exudated from vegetation and dusts. Global natural emissions are estimated up to 7900 tons per year (Plant *et al.* 2003), but anthropogenic emissions – 23600 tons per year (Chen 2011).

Antimony, like arsenic, is a toxic element that occurs in the environment as a result of natural and human activities. Natural sources of antimony include rock weathering, soil runoff as well as geothermal waters. The concentration of antimony in non-polluted natural waters usually is lower than 1 μg/L, in freshwaters – 0.03–10 ng/L; an average concentration of antimony in sea water is 184±45 ng/L, but it may reach 430 ng/L. However, considerably higher concentration of antimony is observed in geothermal waters where, depending from conditions, level of antimony varies from 0.5 to 100 g/L while in polluted areas – close to anthropogenic sources – the concentration of antimony can be up to 100 times higher in comparison with natural levels (Filella *et al*. 2002, Leuz 2006).

Natural levels of antimony in soils and sediments usually are about few μg/g, but higher levels could be related to anthropogenic pollution (Filella *et al*. 2002a).

Content of antimony in aerosols over unpolluted areas (oceans) are lover than 0.1 ng/m^3, but it may reach a number of ng/m^3 over the industrial areas (Filella *et al*. 2002a).

Tellurium is found in low abundances in the environment. Therefore, a number of researches about concentration and forms of tellurium in the environment are small. Average content of tellurium in soils of Europe is 0.03 mg/kg (Perkins 2011). Average concentration of tellurium in rivers is $2.8 \cdot 10^{-3}$ μg/L, in sea water from $5.10 \cdot 10^{-5}$ μg/L to $1.66 \cdot 10^{-4}$ μg/L. However, tellurium content in Fe-Mn crust of Pacific Ocean is 55,000 times higher than its' average content in the Earth crust (Hein *et al.* 2003). Tellurium compounds have been determined in the soil gas derived near ore deposits, also in the geothermal waters (New Zealand), in waste and wastewater gases and in sediments of rivers and ports (Dopp *et al.* 2004).

Inorganic forms of metalloids are predominant in the environment, although up to 1 % of total dissolved forms of metalloids are methylated forms which can be determined in a variety of environmental samples. Methylated forms of As, Sb and Te have been found in geothermal waters at levels of ng/L to μg/L (Dopp *et al.* 2004).

1.2. Speciation forms of metalloids in water

Red-ox potential and pH are the main factors that affect speciation forms of metalloids in water.

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 are more common and toxic than the organic species. Inorganic arsenic is the predominant form in polluted waters, and it exists in two oxidation states – As(III) and As(V), depending on pH and red-ox conditions (Ansari and Sadegh 2007, Pokhrel and Viraraghavan 2006). Arsenite predominates in reduced conditions, but arsenate prevails in an oxidising environment (Pokhrel and Viraraghavan 2006). In medium with pH 3–9 the dominant species of As(III) is neutral H_3AsO_3, while those of As(V) are negatively charged $HAsO_4^{2-}$ and $H_2AsO_4^{-}$ (Nemade *et al*. 2009).

Antimony can occur in a variety of oxidation states (–3, 0, +3, +5) but in environmental, biological and geochemical samples it mainly exists in two oxidation states (+3 and +5). Although, as a result of soil microbial activities, organic forms of antimony, for example, trimethyl antimony ($(CH_3)_3Sb$) can also be produced (Ceriotti and Amarasiriwardena 2009). Like arsenic (V), also Sb(V) is the predominant species in oxic systems but Sb(III) in anoxic systems, although some studies reveal that significant amount of Sb(III) can be also found in oxic and Sb(V) in anoxic systems (Filella *et al*. 2002, Steely *et al*. 2007). Reasons of these occurrences could be related to biological activity or kinetic effects as well as to photochemical reactions and pH (Filella *et al*. 2002, Steely *et al*. 2007). In medium with pH 2–11 antimony exists primarily as antimonate $[Sb(OH)_6]^-$ in oxidizing environments and as antimonite $[Sb(OH)_3]$ in reducing environments (Filella *et al.* 2002). In aqueous solutions Sb(III) is available as $[SbO]^+$ and $[Sb(OH)_2]^+$ species at pH<3. $[HSbO_2]$ and $[Sb(OH)_3]$ species are predominant at pH 3–10 and $[SbO_2]^-$ species is existing in aqueous solution at pH>10 (Uluozlu *et al*. 2010).

Tellurium can exist in four oxidation states (–2, 0, +4 and +6) in the environment. Aqueous Te species mainly exist in the form of oxyanions (TeO_3^{2-}, TeO_4^{2-}) or hydroxide anions ($Te(OH)_6$, $TeO(OH)_3^-$). Te(VI) is the main aqueous species under oxic conditions, whereas Te(IV) predominates under reducing conditions (Harada and Takahashi 2009). It is suggested that $H_5TeO_6^-$ is the predominant form of tellurium in aqueous environment at pH 7.5–11, while H_6TeO_6 is the predominant form at pH<7.7 (Hein *et al*. 2003, Schweitzer and Pesterfield 2009).

1.3. Toxicity of metalloids

Distribution of arsenic, its toxicity, health hazards, remediation and speciation techniques as well as different materials that could be used for arsenic removal have been extensively studied. The main health hazards caused by intoxication of arsenic and its compounds involve cancer of skin, lungs, bladder and kidneys, changes of skin pigmentation and skin thickening, neurological and cardiovascular problems as well as muscular weaknesses (Jain and Ali 2000). Nowadays, contamination of many natural water sources with arsenic is a global problem, especially in Southeast Asia, for example, in Bangladesh, and also in South America, the United States, and Europe (Klemm *et al.* 2005, Moller *et al.* 2009, Smedley and Kinniburgh 2002). Furthermore, drinking water in polluted areas contain dissolved arsenic in quantities above 10 μg/L which is the threshold value, recommended by the World Health Organization, that many nations have adopted as their regulatory standard (Dupont *et al*. 2007, Henke 2009).

Toxicity of arsenic compounds depends on speciation form of arsenic. In addition, As(III) is more toxic, soluble and mobile in biological systems than As(V) compounds (Dupont *et al.* 2007, Nemade *et al*. 2009). The organic forms of arsenic such as monomethyl arsenic acid (MMAA) and dimethyl arsenic acid (DMAA) are rarely present in surface waters in comparison with the inorganic forms. Organic arsenic species occur in natural waters as a result of the use of organo-arsenic pesticides and through the bio methylation mechanism by microorganisms. It is considered that the organic forms of arsenic are less toxic than the inorganic ones (Katsoyiannis and Zouboulis 2002, Thirunavukkarasu *et al.* 2001). Toxicity of arsenic and antimony is caused by ability of As and Sb to react with the sulfhydryl groups of the enzyme system, thus blocking the action of the thiol groups of enzymes (Ansari and Sadegh 2007, Ceriotti and Amarasiriwardena 2009).

Wide use of antimony and tellurium in variety of different products and high technology applications has increased concentration of metalloids in the environment in the recent years as well as more attention is paid to the toxicity of metalloids.

Antimony is used in semiconductors in production of infrared detectors and diodes. Presence of antimony enhances hardness and mechanical strength of lead. Sb is also used in batteries, antifriction alloys, catalysts, small arms, tracer bullets, cable sheathing, brake lining, ant parasitic agents, polyethylene terephthalate plastics and as an additive in the tire vulcanization process, as a flame retardant additive, and elsewhere (Ceriotti and Amarasiriwardena 2009, Filella *et al*. 2002, Steely *et al*. 2007).

Like arsenic, also antimony is a metalloid and, due to its position in the periodic table of elements, its chemical and toxicological properties are similar to arsenic. Antimony and its compounds are considered as pollutants by the Environmental Protection Agency of the United States (USEPA) as well as in the European Union (Filella *et al.* 2002). The maximum admissible concentration of antimony in water is 5 µg/L recommended by EU (Council of the European Union 1998) and 6 µg/L recommended by USEPA. While the maximum admissible concentration of antimony in water is 20 µg/L recommended by WHO (Kyle *et al.* 2011). Antimony, like arsenic, is toxic, and trivalent species are reported to be more toxic than pentavalent species (Ceriotti and Amarasiriwardena 2009, Filella *et al*. 2002,). Solubility of antimony compounds in bio fluids, Sb valence state and presence of complexing agents affects the toxicity of Sb (Ceriotti and Amarasiriwardena 2009, Steely *et al*. 2007). Thus in the human body, antimony may interact with –SH groups in cellular components, a toxic effect of Sb in high doses is observed (Ceriotti and Amarasiriwardena 2009).

Like antimony and arsenic, also tellurium is toxic element and its toxicity can induce local environmental problems. Up to now, there are not many studies done to research behaviour of Te and its compounds in the environment, and the main attention in the existing studies has been focused on tellurium pollution near tailing sites and industrial areas. Tellurium is widely used in petroleum refining, electronic and photoelectric industries as well as glass, ceramics, rubber and alloy production, for example, as an additive on steel and copper to provide machinability (Wang *et al*. 2011, Zhang *et al*. 2010). Similarly like for other metalloids, the toxicity of tellurium is dependent on its chemical form and oxidation state, for example, Te(IV) is about 10 times more toxic than Te(VI) (Harada and Takahashi 2009). Tellurium can accumulate in kidneys, heart, liver and spleen, and if its concentration exceeds 0.002 g/kg, kidney and liver degeneration can be induced (Zhang *et al*. 2010). Organs directly affected by tellurium are kidneys, nervous system, skin and fetus (Taylor 1996).

1.4. Methods and materials used for removal of metalloids

Taking into account toxic properties of metalloids, different treatment approaches to remove metalloids from aqueous systems and to reduce pollution have been developed. Sometimes a number of different methods are used sequentially one after another. Some examples of applied techniques are oxidation, coagulation, precipitation, ion exchange and adsorption (sometimes divided in adsorption and biosorption), membrane processes, electrolysis, solvent extraction, reverse osmosis and cementation (Anirudhan and Unnithan 2007, Dupont *et al*. 2007, Negrea *et al*. 2011, Parga *et al*. 2009, Uluozlu *et al*. 2010, Xi *et al*. 2010). The main disadvantage for majority of the above mentioned techniques is high expenses. It is suggested that adsorption is one of the best methods not only due to its simplicity and potential for regeneration but also because it is economic and easy to set up (Dupont *et al*. 2007, Uluozlu *et al*. 2010, Zhang and Itoh 2005). Among the main disadvantages for adsorption high costs of some specific sorbents can be mentioned. There are several definitions of biosorption that include more or less broad explanation of the process. However, biosorption can be defined as physicochemical and metabolically independent process which is based on several mechanisms involving absorption, adsorption, ion exchange, surface complexation and precipitation (Fomina and Gadd 2014).

Although many different sorbents have been used for metal and metalloid removal so far, due to unsatisfactory efficiency and high costs of these sorbents, opportunities are still open for finding new environmentally friendly and cost effective sorbents. It is worth mentioning that an increasing attention is currently being paid to the development of new sorbents from natural raw materials such as agricultural and industrial waste (Escudero *et al.* 2009). There are numerous sorbents that contain unmodified natural materials, for example, naturally available red soil (Nemade *et al*. 2009), clay minerals (kaolinite (Xi *et al.* 2010), bentonite (Xi *et al*. 2011)), goethite (Wilson *et al.* 2010), lichen biomass (Uluozlu *et al*. 2010), and also sorbents based on natural materials such as iron-modified sand (Guo *et al.* 2007, Thirunavukkarasu *et al*. 2001), Fe(III)-orange juice industrial residue, and iron-modified fungal biomass (Pokhrel and Viraraghavan 2006). Some studies have demonstrated that inorganic forms of arsenic and antimony can strongly bind to Fe-containing compounds. Due to the high affinity of metalloids to iron, different iron-loaded sorbents have been suggested. There are literature studies on goethite, hematite, iron-coated sand, Fe-loaded coral limestone, granular ferric hydroxide, ferrihydrite, pyrite, ferruginous manganese ore, manganese green sand, iron oxide impregnated activated alumina, naturally available red soil, modified (iron (III)-loaded) orange juice industrial residue, modified biomass, iron-oxide-coated polymeric materials, e.g., Fe-XAD7-DEHPA resin and others that are used as sorbents for arsenic removal (Ghimire *et al.* 2002, Guo *et al*. 2007, Katsoyiannis and Zouboulis 2002, Kuriakose *et al*. 2004, Loukidou *et al*. 2003, Manna and Ghosh 2005, Mikutta and Kretzschmar 2011, Negrea *et al.* 2011, Nemade *et al.* 2009, Thirunavukkarasu *et al.* 2001). The solid phases loaded with Fe species may sorb arsenates as well as arsenites, possibly due to the formation of surface complexes as a result of interaction between negatively charged arsenates with $FeOH_2^+$ surface groups (Dupont *et al*. 2007, Payne and Abdel-Fattah 2005). There is also evidence for complex formation between arsenic oxyanions and ferric iron complexes of humic substances (HS). Spectroscopic evidence for ternary complex formation between As(V) and Fe(III)-HS complexes was discovered by Mikutta and Kretzschmar (2011) using Extended X-Ray Absorption Fine Structure spectra (EXAF). A number of studies have investigated the sorption behaviour of Sb on hydroxides of Fe, Mn, Al, humic acids, and clay minerals. Some studies demonstrated that both, Sb(III) and Sb(V), can tightly bind to Fe hydroxides (Leuz *et al.* 2006, Rakshit *et al*. 2011,). Moreover, formation of Sb-O-Fe bonds have been proved using spectroscopic methods after sorption experiments of Sb(V) onto Fe oxides (McComb *et al.* 2007, Xi *et al*. 2010).

2. Materials and methods

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

Diodium hydrogen arsenate heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$; Sigma-Aldrich), sodium arsenite ($AsNaO_2$; Fluka), cacodylic acid ($C_2H_7AsO_2$; Sigma-Aldrich), potassium hexahydroxoantimonate (V) ($KSb(OH)_6$; Fluka), potassium antimony tartrate semi hydrate ($C_4H_4KO_7Sb \cdot 0.5\ H_2O$; Sigma-Aldrich), potassium tellurite hydrate ($K_2TeO_3 \cdot x\ H_2O$; Sigma-Aldrich) and telluric acid (H_6TeO_6; Sigma-Aldrich) were chemicals of analytical grade. Sorption experiments were provided using eight different materials that were modified with Fe(III) hydroxide, involving 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), moss modified with $Fe(OH)_3$, as well as straw, reed, saw dust modified with $Fe(OH)_3$, and also sand modified with $Fe(OH)_3$ was used for comparison.

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. Other materials such as pine (*Pinus sylvestris* L.) saw dust, wheat (*Triticum aestivum* L.) straw, moss (*Sphagnum magellanium*), common reed (*Phragmites australis (Cav.)* Trin. ex Steud.) and sand were also used. Modification of materials involved precipitation of iron hydroxides on the surface of the studied material with following thermal treatment (DeMarco *et al*. 2003, Gu *et al*. 2005, Zhang and Itoh 2005). Hereinafter, these modified materials are marked as Fe-modified biomaterials (Fe-modified peat, Fe-modified moss etc.), whereas in tables and figures abbreviations (mod. peat, mod. moss etc.) are used further in this thesis. 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.

Humic acids (HA) extracted from peat derived from bogs of Latvia as well as Fe-humate were also used in sorption experiments.

2.1. Methods of synthesis

Modification of biomass with iron compounds

Taking into account the affinity of metalloids to interact with Fe-containing compounds, Fe-modified biomaterial sorbents were synthesized. The method of synthesis was based on modified methodology described by DeMarco and colleagues (2003). The method was based on impregnation of a material with Fe hydroxide, followed by thermal treatment. 67.55 g (0.25 mol) $FeCl_3 \cdot 6H_2O$ was dissolved in 250 mL distilled water, after adding 250 mL 3M NaOH and leaving for 4 hours. Then, formed precipitates were rinsed and decanted in a 1 L vessel. Dispersion of $Fe(OH)_3$ was mixed with 100 g of homogenized biomass (peat, saw dust, straw, sand, reed and moss). After filtration, the product of reaction was rinsed with approximately 0.5 L deionized water, filtered, dried and heated for 4 hours at 60 °C. As a result, Fe-modified peat, Fe-modified straw, Fe-modified saw dust, Fe-modified sand, Fe-modified moss and Fe-modified reed were obtained.

Synthesis of iron humate

Commercially produced solution of potassium humate was used for preparation of iron humate. Potassium humate was derived of peat from the Ploce Bog (Latvia). 500 mL 10 % $FeCl_3 \cdot 6H_2O$ was added to the solution of potassium humate, and suspension was mixed and left for 24 h. After that, formed iron humate was filtered off and heated for 4 hours at 60 °C. Then the product was rinsed with 200 mL 1 M NaCl and deionised water, and dried.

2.2. Isolation of humic substance

Humic acids of peat from the Gagu Bog (Latvia) were extracted and purified using procedures recommended by M. Kļaviņš and E. Apsīte (1997). Briefly, 20 g of air-dried and finely ground samples were extracted with 1 L of 1 M NaOH and stirred for 24 h. Suspension was filtered and obtained solution was acidified with conc. HCl to pH < 2 to precipitate humic acids, leaving fulvic acids in solution. Derived humic acids were further purified by repeated dissolution and precipitation as well as dialysis against Millipore water with drying at the end.

2.3. 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 Fe_2O_3.

For determination of organic matter, the loss-on-ignition (LOI) method was used. 1 g of each sample was dried at 105 ºC temperature for 12 h and then burned at 550 ºC temperature in a muffle furnace for 4 h. Samples were weighed after cooling, and content of organic matter was calculated according to LOI (eq. 2.1.) (Heiri *et al*. 2001):

$$LOI_{550} = \frac{DW_{105} - DW_{550}}{DW_{105}} \cdot 100 \qquad (2.1.)$$

where LOI_{550} - LOI at 550 ºC (%), DW_{105} - dry weight of the sample before combustion (g), and DW_{550} – dry weight of the sample after heating at 550 ºC (g).

Content of Fe_2O_3 was determined in samples after heating at 550 ºC. Samples were mineralized using concentrated HCl and conc. HNO_3, and heated at 120 ºC 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). Content of iron (III) oxide in the sorbent was calculated according to the equation 2.2.

$$w_{Fe_2O_3} = \gamma_{Fe} \cdot \frac{M_{Fe}}{M_{Fe_2O_3}} \cdot \frac{V}{m}, \quad (2.2)$$

where γ_{Fe} - concentration of iron in the sample (mg/g), M_{Fe} and M_{Fe2O3} - molecular weight of Fe and Fe_2O_3 (g/mol), 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 made by Spectrum v 5.3.1 software. Samples were pressed in KBr pellets, and the spectra were recorded in the range of 4000-400 cm^{-1} with a 4 cm^{-1} resolution.

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

Surface area of sorbents was measured using a surface area pore size analyser Gemini2360. The Brunauer–Emmett–Teller (BET) method was used for the specific surface area measurements.

Determination on the point of zero charge (pH_{zpc}) was provided using immersion technique (Fiol and Villaescus 2009). 40 mL 0.03 M KNO_3 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 pH was measured. The change of pH (ΔpH) during equilibration was calculated and the pH_{zpc} was identified as the initial pH with minimum ΔpH.

2.4. Data analysis

Experimentally obtained data were processed with MS Excel. Standard deviation as well as safety interval was calculated. Correlation of obtained sorption data was done using the Langmuir and Freundlich isotherm models.

The least square method and MS Excel optimization tool (Solver) were used to obtain theoretical sorption isotherms. Modified Langmuir-1 equation (eq. 2.3.) was used for optimization. It was assumed that sorbents have two sorption centres.

$$q_e = \frac{q_{m1} \cdot k_1 \cdot C_e}{1 + k_1 \cdot C_e} + \frac{q_{m2} \cdot k_2 \cdot C_e}{1 + k_2 \cdot C_e} \quad (2.3.)$$

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

2.5. Sorption experiments

Sorption experiments were conducted using batch system. $Na_2HAsO_4 \cdot 7H_2O$, $NaAsO_2$ and $C_2H_7AsO_2$ were used for preparation of arsenic stock solutions at various concentration of arsenic (300, 200, 100, 50, 25, 10 and 5 mg/L). $KSb(OH)_6$ and $C_4H_4KO_7Sb \cdot 0.5\ H_2O$ were used for preparation of antimony stock solutions at various concentration of Sb (10, 25, 50, 100, 200, 300, 400, 600, 800, 1000 mg/L). H_6TeO_6 and $K_2TeO_3 \cdot x\ H_2O$ were used for preparation of tellurium stock solution at such concentration of Te as 10, 25, 50, 100, 200, 300, 400, 600, 800, 1000 mg/L.

Fe-modified peat, Fe-modified straw, Fe-modified saw dust, Fe-modified sand, Fe-modified moss, Fe-modified reed, Fe-humate and humic substances were used as a sorbent material.

Fe-modified peat and arsenic solution (300 mg/L) were used to detect the optimal sorbent/sorbate ratio. For this reason, four different sorbent concentrations were used (2.5, 6.25, 10 and 12.5 g/L). Sorption experiments were performed in triplicate. It was established that the optimal sorbent concentration in the solution was 12.5 g/L; therefore, this sorbent/sorbate ratio was used in all further experiments.

40 mL of a metalloid solution was added in each 100 mL glass bottle with 0.5 g sorbent. Bottles were shaken for 24 h at room temperature. Suspension was filtered after, and a concentration of metalloid in the filtrate was analysed using Perkin-Elmer atomic absorption spectrometer AAnalyst 600 with graphite furnace (ETAAS – Electrothermal Atomic Absorption Spectrometry). PerkinElmer AAnalyst 200 with flame atomization (FAAS – Flame Atomic Absorption Spectrometry), Perkin Elmer PinAAcle 900F + MHS 15 (Mercury/Hydride system) (HGAAS – Hydride Generation Atomic Absorption Spectrometry) and PerkinElmer ELAN 6000DRC (ICP-MS Inductively Coupled Plasma Mass Spectrometry) were also used for determination of metalloid concentration in filtrates.

Influence of pH on metalloid sorption process

0.1 M NaOH and 0.1 M HCl were used for investigation of pH impact. In glass vessels with 0.5 g of sorbent, 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. Initial concentration of arsenic and tellurium used for the solution was 100 mg/L but initial concentration of antimony was 200 mg/L. Filtrates were analysed with FAAS or ETAAS.

Influence of ionic strength on metalloid sorption process onto Fe-modified peat

For investigation of ionic strength impact arsenic concentration in the solution was 10–300 mg/L but antimony and tellurium concentration was 10–400 mg/L . Three different concentrations of $NaNO_3$ (0.1 M, 0.01 M, and 0.001 M) were used. Sorbent/sorbate ratio was kept as previously mentioned. Filtrates were analysed with FAAS or ETAAS.

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

KH_2PO_4, $NaNO_3$, NaCl, Na_2SO_4, $Na_2C_2O_4$, $C_4H_4KNaO_6 \cdot 7H_2O$, Na_2CO_3, Na_2SiO_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, while the concentration of humic acid was 12.5 mg/L. The initial arsenic concentration varied from 10 mg/L to 300 mg/L, but concentrations of antimony and tellurium varied from 10 mg/L to 400 mg/L. Sorption experiment was continued for 24 h at room temperature. Filtrates were measured using FAAS or ETAAS.

Influence of temperature on metalloid sorption process onto Fe-modified peat

For investigation of impact of temperature on metalloid removal, sorption experiments were carried out at 275 K, 283 K, 298 K and 313 K temperature. Sorbent/sorbate ratio was kept as previously mentioned. Sorption experiment was continued for 24 h. Filtrates were measured using FAAS or ETAAS.

Sorption kinetics of metalloids onto Fe-modified peat

Sorption experiments were performed in the same manner as previously described. Initial arsenic concentration was 100 mg/L, while initial concentration of antimony and tellurium was 200 mg/L. In a 100 mL glass bottle with 0.5 g of a sorbent, 40 mL of metalloid solution was added. Bottles 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. Characterization of sorbents

Wide variety of sorbents has been used for metal and metalloid sorption experiments so far. Industrially produced sorbents as well as natural materials and different modified materials are used as sorbents. Nowadays, selection of a sorbent material mainly is estimated by the sorption capacity and costs of the material. However, one of the targets of sorbent materials is creation them friendly to the environment; therefore, larger attention is paid to sorbents based on natural materials.

Different modification methods are used to enhance sorption capacity of materials. Taking into consideration not only the need for water treatment using cost-effective and environmentally friendly sorbents but also the potential of iron-containing sorbents to interact with metalloids, a possibility of obtaining iron-modified biomass and its use for metalloid removal was examined. The synthesis of iron-modified biomass was based on biomass impregnation with iron hydroxide, followed by thermal treatment. New sorbents were synthesized using widespread, easily accessible materials in Latvia. These sorbents were marked as Fe-modified biomaterials (Fe-modified peat, Fe-modified moss etc.), whereas in tables and figures abbreviations – mod. peat, mod. moss etc. are used further in this thesis.

Content of organic substances as well as moisture content, Fe_2O_3 analysis, nitrogen adsorption isotherm measurements, FT-IR spectra and SEM images were used to characterize the sorbents. Some characteristics of sorbents are given in Table 3.1. Content of organic matter for Fe-modified peat sorbents varied from 72 % to 79 %; similar content of organic matter was detected for Fe-modified saw dust, reed, moss and Fe-modified straw sorbents and it varied from 79 % to 84 %. As it was expected, Fe-modified sand contained a considerably lower content of organic substances in comparison with other Fe-modified sorbents (Table 3.1). 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 %); similarly also content of organic matter in raw material of moss and reed reached 98 %. There were no significant changes observed in the content of C, H, N and O among all used materials.

Obtained results indicated that the applied method of modification was effective, because content of Fe_2O_3 was significantly enhanced after modification. For example, peat layer (50–60 cm) from the Gagu Bog originally contained 4.1 mg/g of Fe_2O_3 while after modification Fe_2O_3 content reached 424.8 mg/g.

Table 3.1

Characterization of sorbents

Sorbent	**LOI, %**	**Elemental content, %**				**Fe_2O_3, mg/g**	**Specific surface area (after BET method), m^2/g**	**pH_{zpc}**
		N	**C**	**H**	**O**			
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
mod. saw dust	83.8	0.1	29.5	4.4	66.0	297.7	45.13	5.5
mod. reed	79.4	0.4	31.2	4.6	63.8	274.8	40.31	7.0
mod. moss	80.6	0.5	31.4	4.7	63.4	256.5	19.14	3.2
mod. straw	79.3	0.2	31.3	2.3	63.2	292.3	–	5.3
mod. sand	1.0	–	–	–	–	49.4	–	–

Fe-modified peat has the highest content of Fe_2O_3, and its specific surface area (obtained by the BET method) is one of the highest in comparison to other Fe-modified sorbents used in this study (Table 3.1). Specific surface area is one of the most important parameters that affect sorption and, taking into account the high affinity among metalloids and 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 has relevant properties that could ensure high sorption capacity and thus it can be effective for removal of metalloids.

pH of the point of zero charge (pH_{zpc}) is one of the parameters that characterize surface chemical properties of studied materials. pH of the point of zero charge is understood as pH above which total surface of a sorbent is negatively charged while at $pH < pH_{zpc}$ surface has a positive charge (Al-Degs *et al.* 2008).

Surface morphology of used sorbents slightly differs (Fig. 3.1). Decomposed plant residues are characteristic to the raw peat material (Fig. 3.1a), and differences of surface morphology between raw and modified peat are clearly obvious when comparing images a and b in Fig. 3.1. Plant residues coated with iron compounds are characteristic to modified peat. Surface morphologies of modified saw dust, modified reed and modified moss are shown in images c, d, and e of Fig. 3.1. SEM images of Fe-modified biomaterials are similar to the surface morphology of Fe-modified peat, thus indicating similar source materials.

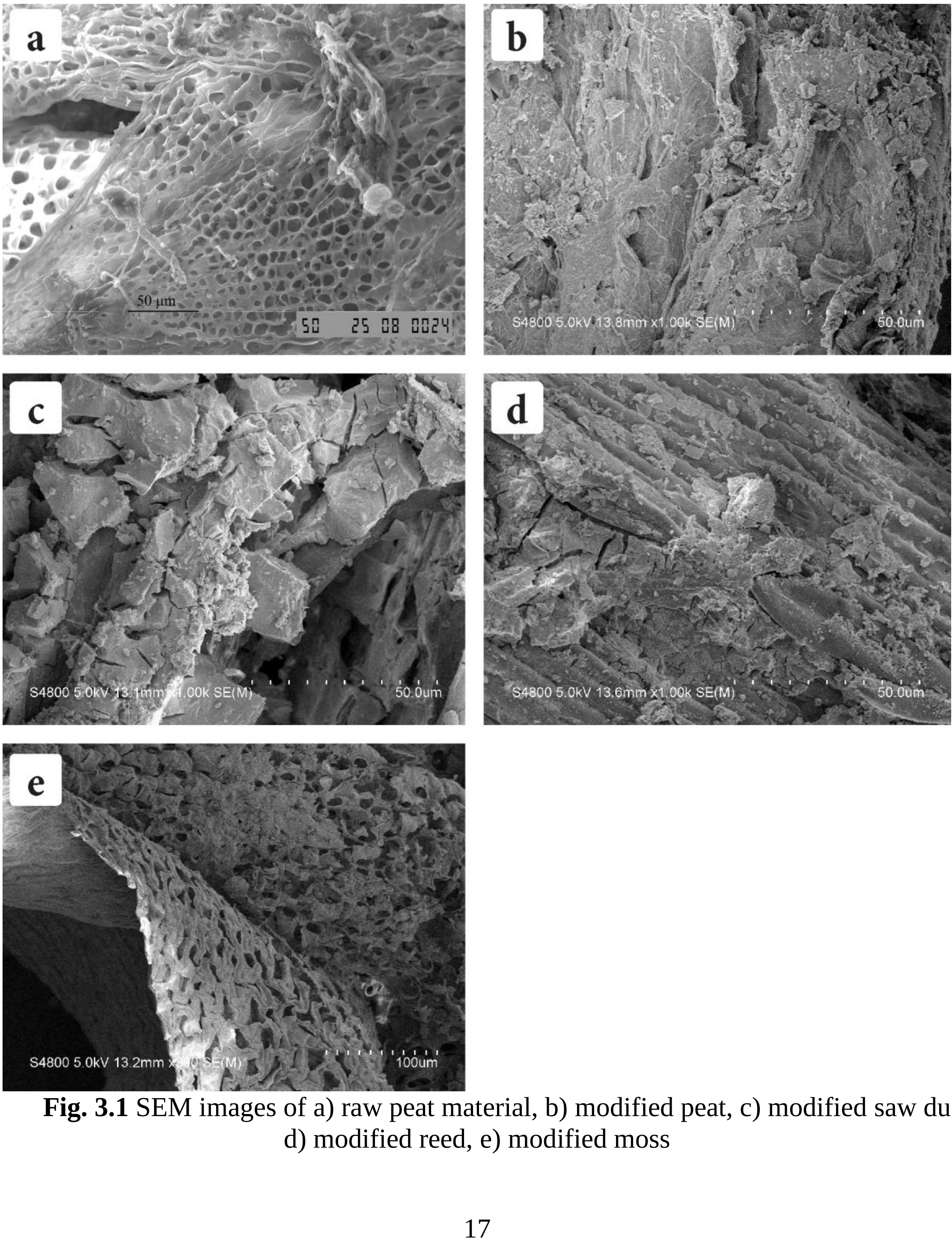

Fig. 3.1 SEM images of a) raw peat material, b) modified peat, c) modified saw dust, d) modified reed, e) modified moss

FT-IR spectrometry is one of the methods that are 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 structural differences in unmodified and modified materials.

Comparing the FT-IR spectra of Fe-modified and raw materials (Fig. 3.2), 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; a band at 3570–3200 cm^{-1} which corresponds to H valence vibrations in hydroxyl groups (Coates 2000). Detected signal at 2900cm^{-1} characterises methine group (>CH-) CH valence vibration, whereas the signal at 1430 cm^{-1} characterises asymmetric/symmetric bends of methyl group (C-H); and at interval 1225–950 cm^{-1} aromatic C-H bend signal was observed (Coates 2000). The signal of FT-IR at 1700 cm^{-1} characterises vibration of carbonyl group that corresponds to carboxylic acids and esters (1700–1725 cm^{-1}), whereas characteristic vibrations of aromatic ring are usually observed at interval 1615–1580 cm^{-1}. The signal at interval 1510–1450 cm^{-1} also characterises vibrations of aromatic ring (C=C-C bonds) (Coates 2000).

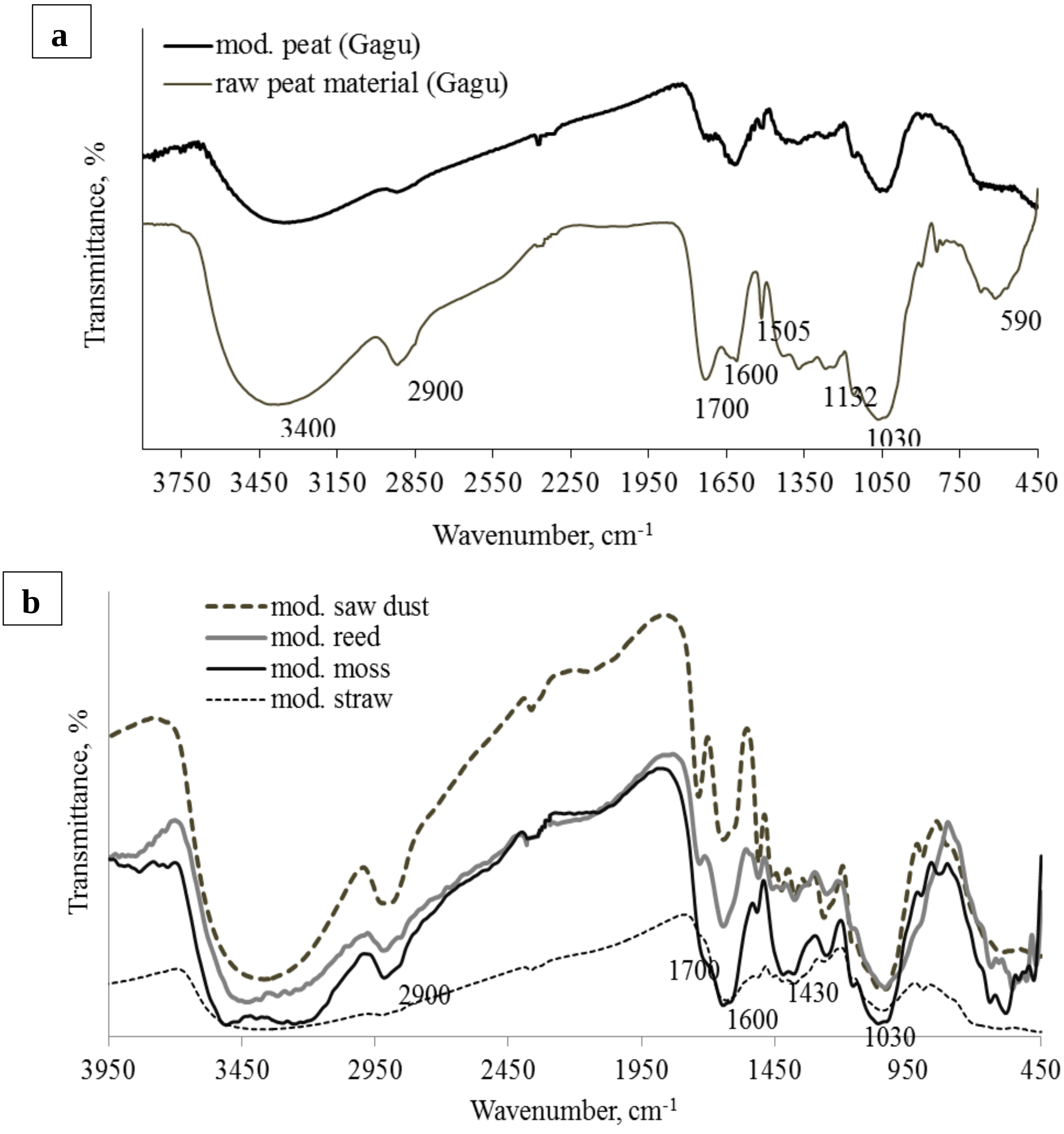

Fig. 3.2 FT-IR spectra of a) Fe-modified peat and raw peat material (the Gagu Bog); b) Fe-modified biomaterials

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 done using program Spectrum v 5.3.1 and relation of band intensities at 1700 and 1600 cm^{-1} were used to compare appropriate signals of functional groups before and after material modification. Obtained results are in agreement with previous studies discussed in literature, for example, in the report done by P. Rodriguez-Lucena with colleagues (2009), 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. 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 aromatic ring, skeletal vibrations of aromatic C=C, and vibrations of C-O, C-C and C-OH (Rodriguez-Lucena *et al*. 2009).

Carboxylic, hydroxyl and amino groups probably could be the main functional groups that can interact with metalloids; and this could explain sorption of metalloids on unmodified materials (peat, straw, saw dust, moss, and reed), while the metalloid-O-Fe bond could support interaction between metalloids and Fe-modified biomaterials (mod. peat, mod. saw dust, etc.).

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. Investigation of sorption of V and VI group metalloids on modified biomaterial sorbents

Sorption experiments were carried out using unmodified materials (three different peat materials, sand, straw, saw dust, moss, reed, humic acid) as well as iron-modified biomass sorbents, Fe-modified sand and Fe-humate. Inorganic forms of arsenic, with oxidation state +3 and +5, as well as organic arsenic form with oxidation state +5, inorganic forms of antimony with oxidation state +3 and +5 and inorganic forms of tellurium with oxidation state of +4 and +6 were used to investigate removal of metalloids.

Sorbed amount of a metalloid (q_e) was calculated according to equation 3.1.

$$q_e = \frac{C_0 - C_e}{m} \cdot V, \qquad (3.1.)$$

where C_0 – initial metalloid mass concentration (mg/L); C_e – equilibrium concentration (mg/L); m – mass of the sorbent (g) and V – volume (L) (Horsfall and Spiff 2005).

Sorbed amount of a metalloid (Q_e) was calculated according to equation 3.2.

$$Q_e = \frac{q_e \cdot 100}{\frac{C_0 \cdot V}{m}}, \qquad (3.2.)$$

where Q_e – sorbed amount of metalloid (%) and q_e – sorbed amount of metalloid (mg/g).

As it was mentioned previously, essential importance should be paid to the content of Fe in sorbents. To evaluate the impact of Fe content on sorption capacity five modified peat sorbents with different Fe content were synthesized. In all cases peat from the Gagu Bog was used. The product yield, content of organic substances and Fe_2O_3 are given in Table 3.2.

Table 3.2

Characterization of Fe-modified peat sorbents depending on the used amount of $Fe(OH)_3$

$Fe(OH)_3$, mol	Product yield, g	LOI, %	Fe_2O_3, mg/g	Specific surface area, (after BET method), m^2/g
0.005	9.36	97.9	49	–
0.01	9.99	94.6	60	–
0.015	10.43	88.0	166	–
0.025	11.94	79.0	252	47.17
0.04	13.80	70.6	350	21.88

Content of Fe compounds that is present in a sorbent has significant effect on sorption capacity of the sorbent. Sorbed amount of metalloids (As, Sb, Te) is increasing (using Fe-modified peat sorbents) with increase of content of $Fe(OH)_3$ from 0.005 mol to 0.025 mol per 10 g of peat that was used in the synthesis of sorbent (Fig. 3.3). Although the highest amount of $Fe(OH)_3$ that was used in the synthesis of sorbents was 0.04 mol per 10 g of peat, this material does not show the highest sorption capacity. It is possible to make an interpretation taking into account specific surface area which is lower than in the sorbent where added amount of $Fe(OH)_3$ was 0.025 mol per 10 g of peat. With increase of the degree of surface modification of the sorbent, dense layer of Fe compound is forming on the matrix (for example, in peat), and as a result the surface area of the sorbent is decreasing similarly like sorption capacity.

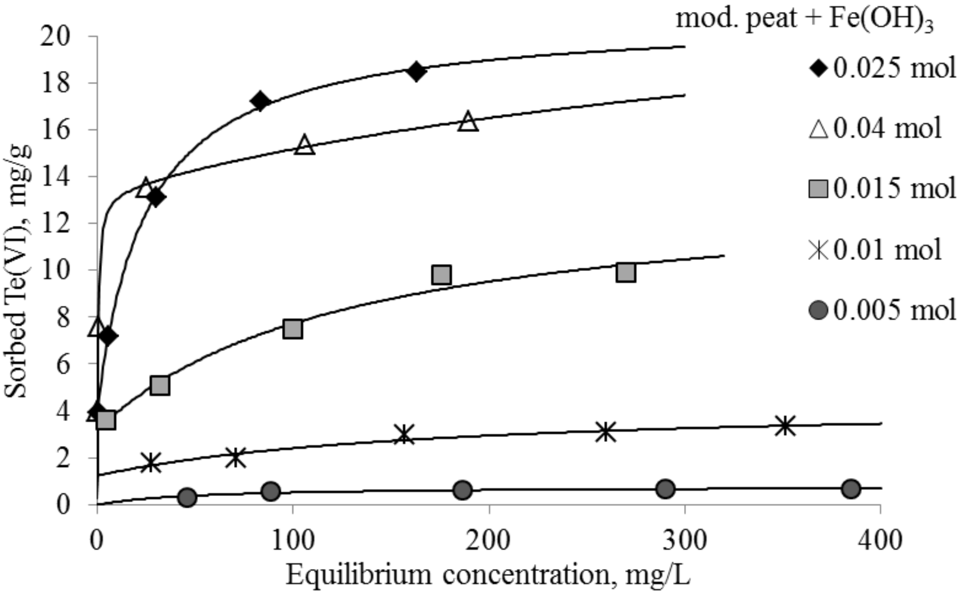

Fig. 3.3 Sorption of Te(VI) depending on the content of Fe in Fe-modified peat sorbents, Te(VI) initial concentration 50–400 mg/L, sorption time 24 h at room temperature

In all further experiments constant weight of the sorbent (12.5 g/L) and content of $Fe(OH)_3$ (0.025 mol) in Fe-modified peat was used applied. Accuracy of the data was evaluated by performing three replicates of every sorption experiment.

Concentration of metalloids in filtrates was determined using different methods (FAAS, ETAAS, HGAAS and ICP-MS). Experimentally determined concentration of metalloids as well as calculated sorbed amount of metalloids are comparable values; thus it is possible to use effectively all previously mentioned methods for the analysis of studied metalloid concentration interval.

3.2.1. *Sorption efficiency of different sorbents*

After the modification of peat with Fe compounds it was managed to enhance the sorption capacity of the material. Three different types of peat were used for As(V) sorption. Sorbed amount of arsenic differs, but in all cases it was considerably higher for Fe-modified peat in comparison with raw peat material. 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. 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.

Obtained data indicated that sorption capacity depends on the biomass 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 reached 15.11 mg/g (Fig. 3.4), i.e., this sorbent may sorb more than 90 % of As(V) at the initial As(V) concentration of 179 mg/L; ability for sorption is reduced to 70 % at the initial As(V) concentration of 269 mg/L. Reduction of sorption ability of the sorbent with increasing concentration of metalloid is affected by Fe/As ratio because increasing concentration of metalloid causes reduction of the number of free sorption sites. Similar sorption ability have Fe-modified moss, Fe-modified saw dust and Fe-modified straw for which sorption capacity reaches 11.36 mg/g, 9.62 mg/g and 9.09 mg/g, respectively. Fe-humate has lower sorption ability (5.20 mg/g). It is possible to remove small amounts of As(V) using Fe-modified reed and humic acids.

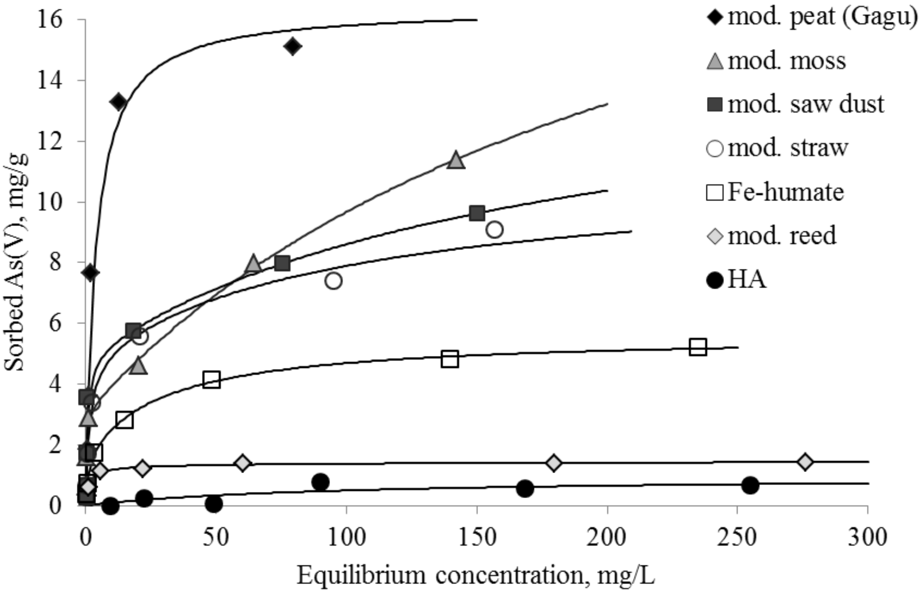

Fig. 3.4 Removal of As(V) using Fe-modified biomass, Fe-humate and humic acid, initial concentration of As(V) 10–300 mg/L, sorption time 24 h at room temperature

Fe-modified biomaterial sorbents and also humic acid 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). It may remove more than 90 % of As(III) at the initial As(III) concentration of 192 mg/L but its sorption ability is reduced to 60 % if the initial As(III) concentration reaches 928 mg/L. 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 and 20.4 mg/g, respectively. Fe-modified saw dust and Fe-modified moss have similar sorption capacity (27.6 mg/g and 25.9 mg/g, respectively). These sorbents may remove up to 90 % of As(III) if the initial As(III) concentration does not exceed 190 mg/L. Fe-modified straw may remove up to 98 % of As(III) at the initial As concentration of 89 mg/L, but Fe-modified reed sorb 92 % As(III) at the initial As(III) concentration of 45 mg/L. Fe-modified sand can be an effective sorbent for As(III) removal only if the initial As concentration does not exceed 25 mg/L. Experimentally obtained data indicated the ability of humic acid to interact with As(III) but it is considerably lower than sorption ability for Fe-modified sorbents (below 22 %).

Studied types of sorbents are also able to remove organic form of arsenic As(org.). The oxidation state of arsenic is +5. Sorption capacity of the sorbents are slightly lower sorbing As(org.) in contrast to As(V). The highest sorption ability applies to Fe-modified peat – its sorption capacity reaches 11.45 mg/g. Fe-modified peat may sorb more than 90 % of As(org.) at the initial As(org.) concentration of 25 mg/L. Similar sorption ability is a characteristic to Fe-modified saw dust, Fe-modified moss, Fe-modified straw and Fe-modified reed. Fe-modified saw dust and Fe-modified moss could be effectively used if the initial As(org.) concentration does not exceed 50 mg/L, then sorption capacity will reach 75 %.

In comparison to arsenic (Fig. 3.4), removal of antimony (V) using Fe-modified biosorbents is considerably more efficient (about two times higher) (Fig. 3.5). Sorption capacity of Fe-modified peat reaches 40 mg/g at the initial Sb(V) concentration of 730 mg/L. Fe-modified peat can sorb up to 95 % of Sb(V) at the initial Sb(V) concentration of 370 mg/L, but it lower (only up to 75 %) at the initial Sb concentration of 730 mg/L. Results for Fe-modified moss as well as Fe-modified saw dust show similar levels of sorption capacity, although the values are not as high as using Fe-modified peat. Sorbed amount of Sb(V) by modified moss and modified saw dust exceeds 95 % at the initial Sb(V) concentration of 90 mg/L, and it decreases to 48 % and 41 % at initial Sb(V) concentrations of 556 and 580 mg/L, respectively for modified moss and modified saw dust. Modified straw can sorb up to 57 % of Sb(V) if the initial antimony concentration is 92 mg/L. However, like it was observed in the case of arsenic, Fe-modified reed and Fe-modified sand are less effective sorbents, although the sorption capacity of modified reed and modified sand are greater for antimony than for arsenic.

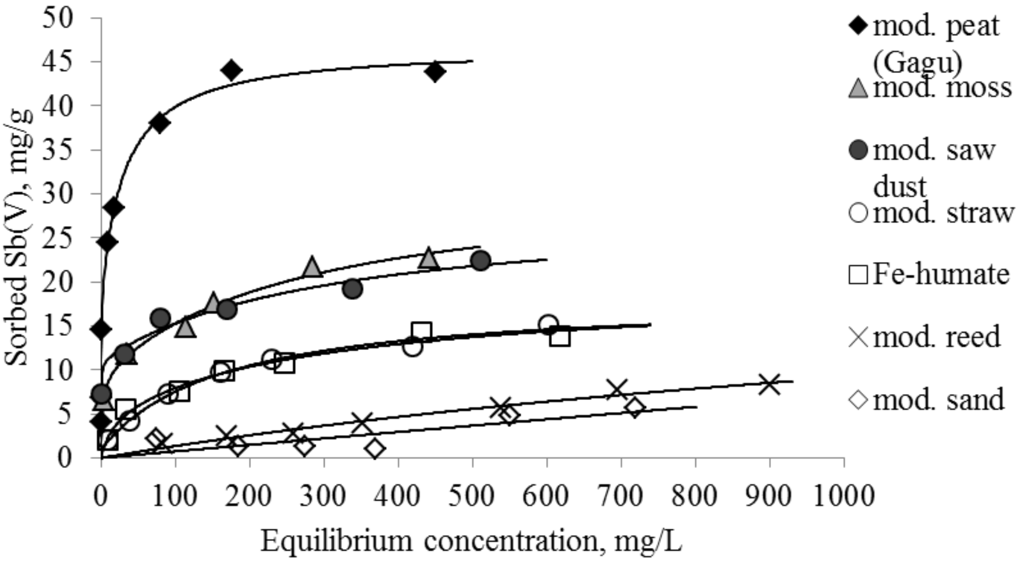

Fig. 3.5 Removal of Sb(V) using Fe-modified biomass and Fe-humate, initial concentration of Sb(V) 10–1000 mg/L, sorption time 24 h at room temperature

Fe-modified peat can effectively remove Sb(III), its sorption capacity reaches 32 mg/g. Fe-modified peat can sorb up to 94 % at the initial Sb(III) concentration of 365 mg/L, but the sorbed amount of Sb(III) decreases to 57 % if initial Sb(III) concentration reaches 702 mg/L. The highest sorption capacity of Sb(III) was observed for Fe-modified peat sorbent. Although Fe-modified reed and Fe-modified sand sorbents are not enough effective for sorption of As, they have ability to remove Sb(V) and they are among the most effective sorbents for removal of Sb(III). The amount of sorbed Sb(III) for Fe-modified reed and Fe-modified sand exceed 97% and 59%, respectively, if the initial Sb(III) concentration is 176 mg/L, whereas sorption capacity of Fe-modified moss and Fe-modified saw dust exceeds 95 % and 83 %, respectively, if initial Sb(III) concentration is 283 mg/L. However, modified straw can be used effectively at lower concentration of Sb(III) as its sorption capacity exceeds 40 % at the initial Sb concentration of 280 mg/L. Relatively high sorption ability is a characteristic to humic acids. They may remove 88 % of Sb(III) if initial Sb(III) concentration is 84 mg/L, thus indicating possible complex formation between HA and Sb(III).

Results obtained for Fe-modified peat, Fe-modified moss and Fe-humate show relatively similar sorption ability for Te(IV) (Fig. 3.6). Moreover, sorption capacity of all these three sorbents reaches 40 mg/g. Sorbents may remove up to 90 % of Te(IV) at the initial Te(IV) concentration of 380 mg/L. Fe-modified straw and Fe-modified saw dust can remove 90 % of Te(IV) if the initial Te(IV) concentration is 280 mg/L, while Fe-modified reed can sorb up to 73 % of Te(IV) if the initial concentration of Te(IV) does not exceed 190 mg/L.

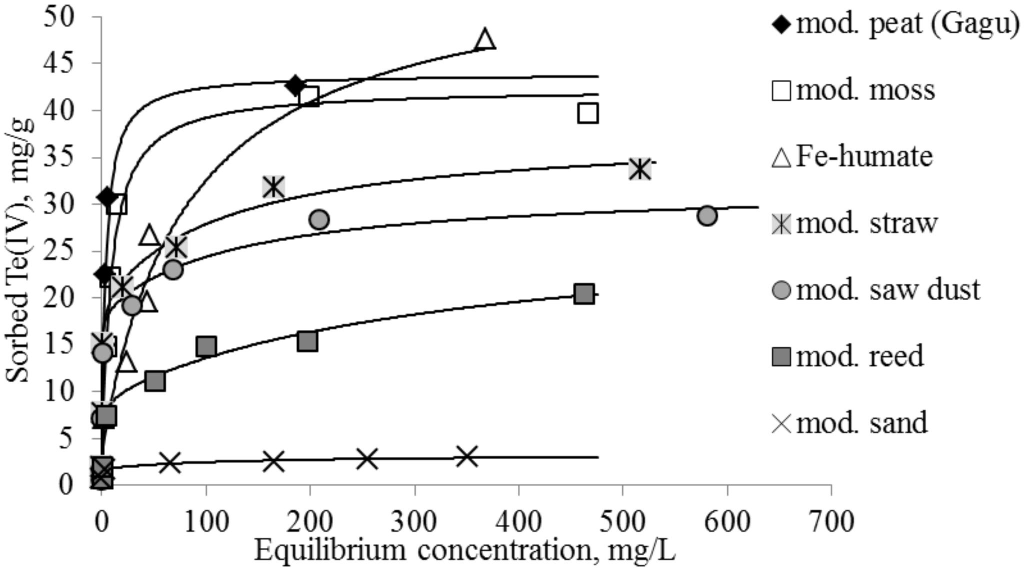

Fig. 3.6 Removal of Te(IV) using Fe-modified biomass and Fe-humate, initial concentration of Te(IV) 10–1000 mg/L, sorption time 24 h at room temperature

In case of Te(VI) sorption capacity of all Fe-modified sorbents, except for modified sand, is similar and varies from 14 to 18 mg/g. Fe-modified peat, Fe-modified moss and Fe-modified reed can sorb about 55 % of Te(VI) at the initial Te(VI) concentration of 400 mg/L, and if the initial concentration of Te(VI) decreases to 100 mg/L, the amount of sorbed Te(VI) reaches 90 %. Similar trend was observed also for Fe-modified saw dust and Fe-modified straw which can sorb about 47 % of Te(VI) at the initial Te concentration of 400 mg/L, but the sorbed amount increases to 95 % and 93 %, respectively, if the initial Te(VI) concentration is 100 mg/L. Fe-modified sand is the inefficient sorbent for Te(VI) in comparison with other sorbents used in this study. It can sorb only up to 70 % of Te(VI) at its initial concentration of 25 mg/L.

In summary, sorbents synthesized in this study can be used for removal of metalloids (As, Sb, Te). Fe-modified peat is the most effective sorbent for all forms of metalloids. It is possible to use Fe-modified peat 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 with diverse their own 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). Fe-modified saw dust and Fe-modified moss can also be effectively used for the removal of metalloids. Fe-modified straw, Fe-humate, Fe-modified reed and Fe-modified sand have high efficiency for sorption of some forms of metalloids and these sorbents are useful for sorption of other forms of metalloids in cases when concentration of metalloid is low (less than 10 mg/L).

Sorption capacity of sorbents varies at sorption of different metalloids such as As(V), Sb(V) and Te(VI). It 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 tetrahedral oxoanion, but antimonate is octahedral oxoanion, wherewith molecules of antimonate have larger ionic radii and lower charge density.

3.2.2. Sorption model of V and VI group metalloids on modified biomaterials

The results of sorption experiments often are compared with theoretical sorption models such as Langmuir, Freundlich, Dubinin-Radushkevich, Redlich-Peterson model and others (Febrianto *et al.* 2009, Ho 2006, Kinniburgh 1986). Obtained sorption isotherms for arsenic, antimony and tellurium were compared using Langmuir and Freundlich sorption isotherm models.

Langmuir equation (Eq. 3.3.) is used to characterize equilibrium between sorbed metal ions and metal ions in the solution. To determine appropriate isotherm linear form of equation is often used. It is possible to linearize Langmuir equation in four different types. However, Langmuir-1 equation (Eq. 3.4.) is the most popular and the most appropriate for the assessment of experimental data.

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \tag{3.3.}$$

$$\frac{C_e}{q_e} = \frac{1}{q_m K_a} + \frac{C_e}{q_m} \tag{3.4.}$$

where C_e is the equilibrium concentration (mg/L); q_e is the amount of arsenic sorbed onto solid phase (mg/g); q_m and K_a are Langmuir constants which are related to sorption capacity and sorption energy, respectively, according to Anirudhan and Unnithan 2007, Kuriakose *et al.* 2004. Moreover, q_m is q_e for a complete monolayer (mg/g) and K_a is the sorption equilibrium constant (L/mg) (Ho and Ofomaja 2005).

To obtain more complete concept about sorption mechanism different sorption parameters are used. For instance, adsorption intensity or without unit equilibrium parameter (R_L), that is linked with Langmuir equation. It is possible to calculate equilibrium parameter using equation 3.5.

$$R_L = \frac{1}{1 + KC_0} \tag{3.5.}$$

where C_0 is initial concentration of metalloid (mg/L) and K is Langmuir constant.

Values of the equilibrium parameter for all studied sorbents sorbing different forms of metalloids vary from 0.004 to 0.79. If R_L values are in the limits of $0 < R_L < 1$, sorption process is evaluated as favourable. Although sorption ability of sorbents is calculated differently, R_L values are in the limits between 0 and 1, thus indicating favourable sorption conditions.

Freundlich sorption isotherm model (Eq. 3.6.) is one of the most often used models.

$$q_e = kC_e^{\frac{1}{n}} \tag{3.6.}$$

where k and n are Freundlich constants which correspond to adsorption capacity and adsorption intensity, respectively. In the base of Freundlich model there is an assumption that sorption surface is heterogeneous and sorption sites have diverse energy. Obtained data can be linearized using linear Freundlich equation (Eq. 3.7.).

$$\log q_e = \frac{1}{n} \log C_e + \log K \tag{3.7.}$$

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 biomaterials as sorbents better fitted to the Langmuir isotherm model, but values of 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.

Studied sorbents are not homogenous; therefore, it is possible that sorbents have more than one sorption centre. Optimization was performed according to the equation 2.3., whereof Langmuir isotherm model constants – q_{m1}, q_{m2} and k_1, k_2 which correspond to sorption capacity of each sorption site and sorption energy were determined.

Sorption of Fe-modified biomaterials can be explained with forming of metalloid-O-Fe bond indicated by values of q_{m1} and k_1. The highest sorption energy (k_1) is a characteristic of Fe-modified saw dust sorbing Te(VI). Theoretically very high sorption capacity (q_{m1}) is obtainable for Fe-modified peat (Gagu) and Fe-modified saw dust sorbents sorbing As(III), though their sorption energy is negligible. Also the second sorption centre has important significance indicated by q_{m2} and $k_{2.}$ 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. Influencing factors of sorption

3.3.1. pH impact on sorption of metalloids

The effect of pH is one of the most important factors that influence 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, while arsenite species is neutral (H_3AsO_3). Stable species of As(V) and appropriate pH values are as follows: H_3AsO_4 (pH 0–2), $H_2AsO_4^-$ (pH 2–7), $HAsO_4^{2-}$ (pH 7–12), and AsO_4^{3-} (pH 12–14) (Mohan and Pittman 2007, Nemade *et al.* 2009).

Sorption capacity of Fe-modified peat sorbing As(V) and As(org.) is maximal at acidic pH values and much lower at alkaline pH values (Fig. 3.7). Fe-modified peat may sorb more than 98 % of As at the initial As concentration of 100 mg/L, at the pH interval 3.2–6.4 but with the increase of pH to 8.14, sorbed amount of As is reduced to 70 %. Whereas As(III) can be effectively removed using Fe-modified peat in a wide pH interval. Fe-modified peat sorbs more than 95 % of As(III) at pH interval 2.76–6.96 and sorption ability reduces to 88 % at pH 9.9 (initial As(III) concentration 100 mg/L).

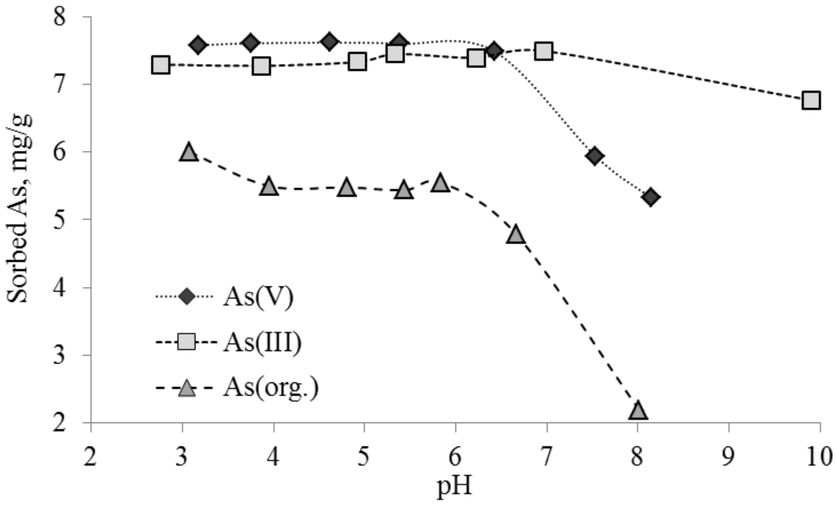

Fig. 3.7 Influence of pH on removal of arsenic using Fe-modified peat as sorbent, sorption time 24 h at room temperature, initial concentration of As – 100 mg/L

However, similar trend was observed also for sorption of other Fe-modified materials. The best sorption conditions are observed at pH interval 3–6.5 for As(V) when $H_2AsO_4^-$ is the predominant form in the solution. It can be supposed that the sorption of As(V) onto Fe-modified materials mainly occur 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 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 $-FeOH_2^+$ and the arsenate ions which leads to the formation of surface complexes (Dupont *et al.* 2007, Payne and Abdel-Fattah 2005).

Surface charge of the sorbent is one of the most important parameters that may characterise protonation and deprotonation, and thus it gives significant information about the mechanism of sorption. As it was previously mentioned, pH of the point of zero charge (pH_{zpc}) is one of the parameters that characterize surface chemical properties of studied materials. The pH_{zpc} is pH above which total surface of the sorbent is negatively charged while at $pH < pH_{zpc}$ the surface has a positive charge (Al-Degs *et al.* 2007). As it is was summarized in Table 3.1, pH_{zpc} values of studied sorbents varies from 3.2 to 7.0, for example, pH_{zpc} of Fe-modified peat is 4.7, it means that the surface of the sorbent is positively charged if $pH < 4.7$, but arsenate has a negative charge, and therefore the sorption capacity is maximal. At $pH > 4.7$, the surface of the sorbent becomes negatively charged and interaction between active sorption sites on the sorbent and negatively charged $H_2AsO_4^-$ and $HAsO_4^{2-}$ ions decreases. The reason for decrease of the sorption capacity in alkaline solution also could be a competition for sorption sites between arsenate and hydroxide ions.

pH_{zpc} is valuable parameter, but not always it can explain pH impact on sorption capacity because natural materials are not homogeneous as well as different other factors may influence sorption capacity, for example, particle size and predominant functional groups of sorbents.

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. Obtained results are in agreement with similar studies (Partey *et al.* 2008).

For Sb(III), the corresponding species are $[SbO]^+$ and $[Sb(OH)_2]^+$ at $pH < 3$, $Sb(OH)_3$ and $HSbO_2$ at pH interval 3–10, and $[SbO_2]^-$ at $pH > 10$ (Uluozlu *et al.* 2010). Whereas predominant form of Sb(V) at pH interval 2–11 is $Sb(OH)_6^-$ (Xi *et al.* 2011). The highest sorption capacity of the studied sorbents sorbing Sb(III) is at the pH interval 6–9 where predominant form is neutral Sb(III). Obtained results are in agreement with other studies (Biswas *et al.* 2009, Buschmann and Sigg 2004, Sari *et al.* 2010). Interaction mechanisms between Sb(III) and Fe-modified sorbents can involve ligand exchange and negatively charged complex formation.

Similarly like in the case of arsenic, the best pH interval for removal of antimony (V) is pH 2–5.5 when $Sb(OH)_6^-$ is the predominant form. Sorption capacity is decreasing at $pH > 5.5$. The reason for decrease of sorption capacity in alkaline solution could be a charge repulsion between negatively charged surface groups of the sorbent and negatively charged Sb(V) ions as well as competition for sorption sites between antimonate and hydroxide ions is possible.

pH has no significant impact on both, removal of Te(IV) (Fig. 3.8) and Te(VI), at the studied conditions. As previously suggested, $H_5TeO_6^-$ is the main form of tellurium (VI) in aqueous environment at pH range 7.5–11, while H_6TeO_6 is the predominant form at $pH <7.7$. Fe-modified peat and Fe-modified moss may sorb more than 95 % of Te(VI) at the initial Te concentration of 100 mg/L, at the entire studied pH interval. The sorbed amount of Te(VI) increases from 55 to 90 % with the increase of pH from 3 to 6 using Fe-modified saw dust; similar trend was observed also for Fe-modified straw. Fe-modified biomaterials may sorb more than 98 % of Te(IV) (Te 100 mg/L) at pH interval 3–7, and sorbed amount of Te(IV) only slightly decreases at $pH >7$.

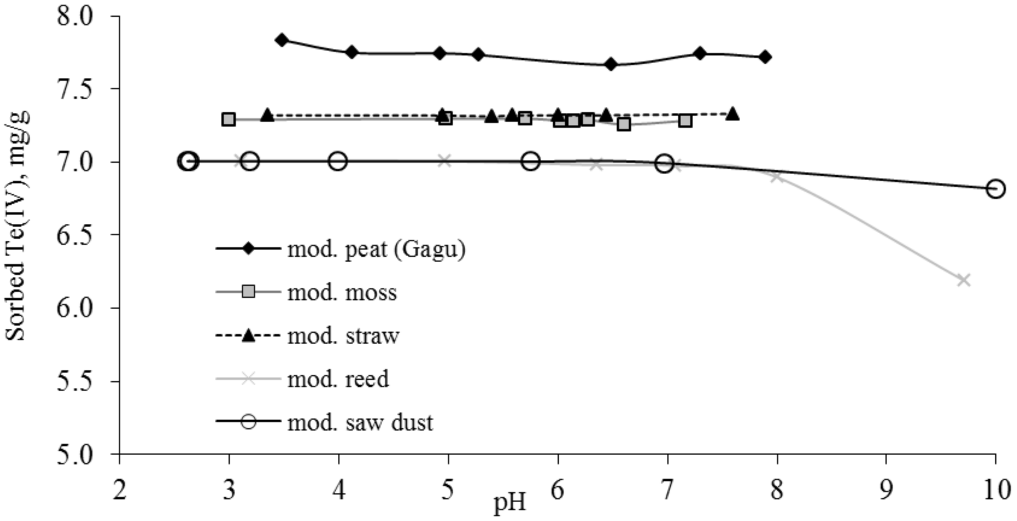

Fig. 3.8 Influence of pH on sorption of Te(IV) using Fe-modified biomaterials as a sorbent, sorption time 24 h at room temperature (initial concentration of Te(IV) 100 mg/L)

In overall, sorption ability of studied sorbents sorbing As(V) and Sb is affected by pH of solution, but impact is weaker in a case of As(III) and Te. Electrostatic interaction could be in a basis of As(V) and Sb(V) sorption on Fe-modified sorbents. Whereas ligand exchange and oxygen bond formation and interaction with Fe compounds could be in a basis of As(III), Sb(III) and Te sorption on Fe-modified sorbents.

3.3.2. Influence of ionic strength on sorption of metalloids on Fe-modified peat

The effect of ionic strength on the sorption of metalloids on Fe-modified peat was studied using sodium nitrate solution as an electrolyte at various concentrations (0.001 mol/L, 0.01 mol/L, 0.1 mol/L). The impact of ionic strength on sorption process of metalloid can give valuable information about sorption mechanism, for example, it can point to formation of inner or outer sphere complexes.

The increase of concentration of sodium nitrate from 0.001 to 0.1 mol/L enhances the sorption of As(V), Sb(III), Sb(V) (Fig. 3.9.) and both, Te(IV), and Te(VI), on Fe-modified peat. While increase in sodium nitrate concentration decreases sorbed amount of As(III).

The anions that form outer sphere complexes are sensitive to the presence of weakly sorbing anions, for instance, nitrate anions. Nitrate anions may suppress metalloid sorption by competing for the sorption of outer-sphere complexes through electrostatic forces. On the contrary, the anions sorbing through inner sphere complexes show either low sensitivity to ionic strength or sorbed amount is increasing with increase of ionic strength (Mahmood *et al.* 2012). Obtained results point to the formation of inner-sphere complexes at the water-solid interface of Fe-modified peat sorbing As(V), Sb(III), Sb(V), Te(IV) and Te(VI), because in all previously mentioned cases the amount of sorbed metalloids increases with the increase of ionic strength.

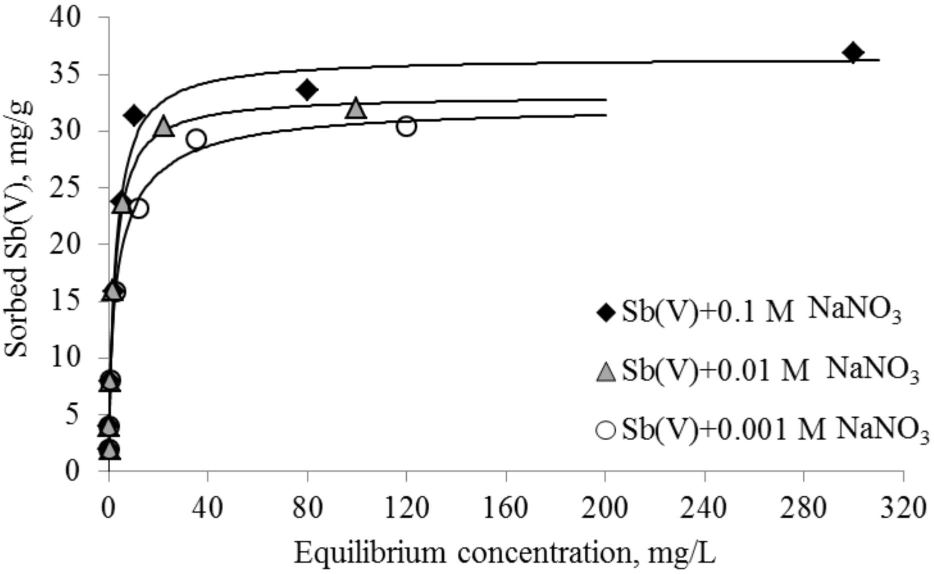

Fig. 3.9 Influence of ionic strength on sorption of Sb(V) using Fe-modified peat as a sorbent, initial concentration of Sb(V) 25–800 mg/L, sorption time 24 h at room temperature

Sorption capacity of Fe-modified peat decreases sorbing As(III) with the increase of ionic strength. Possible reason for it could be a formation of outer-sphere complexes or formation of ion pair surface complexes. Electrolyte ions can compete with sorbed metalloid ions for sorption sites and thus it can negatively affect sorption of As(III) on Fe-modified peat. Among other reasons electrostatic interaction can be mentioned, because enlarged concentration of sodium nitrate can inhibit access of metalloids to the surface of the sorbent thus decreasing sorption rate (Sari *et al*. 2010).

3.3.3. Influence of competing substances on sorption of metalloids on Fe-modified peat

Since Fe-modified peat 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_2PO_4, $NaNO_3$, NaCl, Na_2SO_4, $Na_2C_2O_4$, $C_4H_4KNaO_6 \cdot 7H_2O$, Na_2CO_3, Na_2SiO_3) as well as humic acid (isolated from peat taken from the Gagu Bog, Latvia) were selected. Results indicated that sulphate, nitrate, chloride and tartrate anions have a minor influence on sorption of As(V) onto Fe-modified peat (Fig. 3.10). Obtained sorption capacity for Fe-modified peat was 15.11 mg/g, whereas in the presence of SO_4^{2-} anions it was 13.67 mg/g, and in the presence of NO_3^-, Cl^- and tartrate anions – 13.12 mg/g, 15.01mg/g and 13.3 mg/g respectively. The results of this study are in agreement with the research done under the supervision of Y. Zhang (2003), 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. 3.10). Sorption capacity decreased to 11.04 mg/g 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 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.

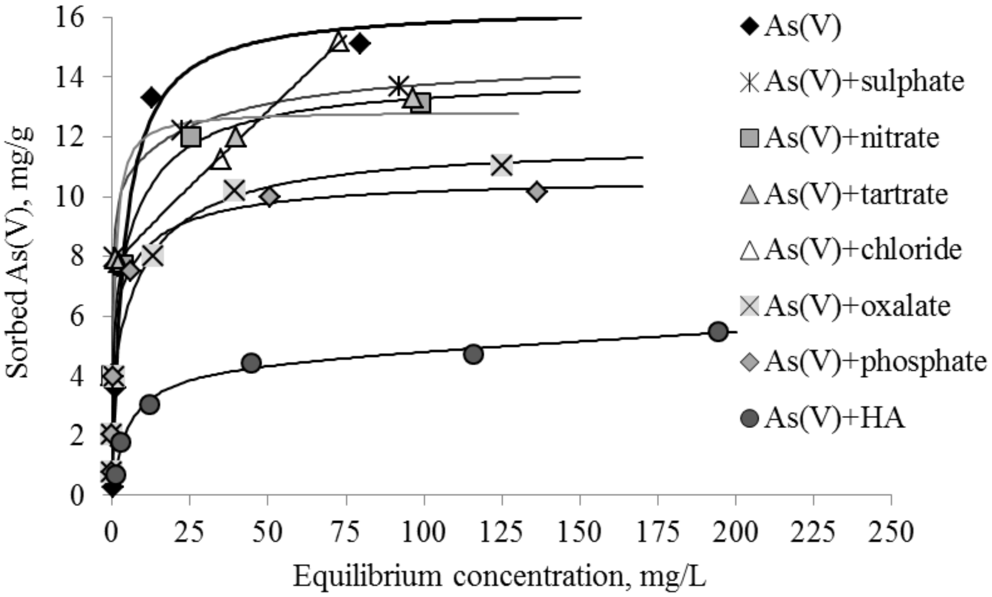

Fig. 3.10 Influence of competing substances on sorption of As(V). Sorbent – Fe-modified peat (from the Gagu Bog), initial concentration of As(V) 5–300 mg/L, concentration of competing ions – 25 mg/L, C_{HA} – 12.5 mg/L, sorption time 24 h at room temperature

Sorption capacity of Fe-modified peat was 5.50 mg/g 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 decrease of sorption capacity in experiments in natural environment in comparison with laboratory experiments, e.g., it was confirmed by studies where tap water and groundwater in Mongolia was used (Zhang *et al.* 2003). 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, (Giasuddin *et al*. 2007).

Similarly like it was observed at sorption experiment with As(V), also removal of Sb(V) is slightly reduced in the presence of tartrate, carbonate and silicate, while sorbed amount of Sb(V) was considerably decreasing in the presence of oxalate and phosphate ions (Fig. 3.11). In contrast to As(V), 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.

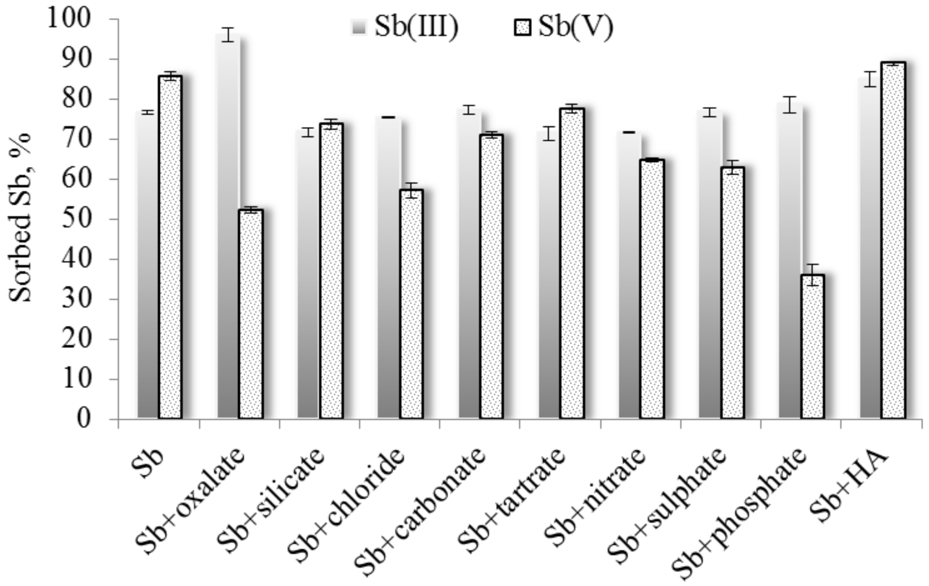

Fig. 3.11 Influence of competing substances on sorption of Sb. Sorbent – Fe-modified peat (from the Gagu Bog), initial concentration of Sb(III) – 530 mg/L, Sb(V) – 590 mg/L, concentration of competing ions – 25 mg/L, C_{HA} – 12.5 mg/L, sorption time 24 h at room temperature

Sorbed amount of Sb(III) on Fe-modified peat did not reduce in the presence of competing substances. 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 (Buschmann and Sigg 2004, Sh *et al.* 2012).

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, but removal of Te(IV)was reduced to 98 %, 81 % and 80 % in the presence of chloride (25 mg/L), phosphate (25 mg/L) and carbonate (25 mg/L), respectively. Sorbed amount of Te(IV) reduced to 72 % in the presence of tartrate (25 mg/L), silicate (25 mg/L) and oxalate (25 mg/L). Sorbed amount of Te(IV) is substantially affected by the presence of HA when 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 initial Te(VI) concentration of 390 mg/L. However, 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 %).

In overall, competing ions as well as HA affect sorption of metalloids on Fe-modified peat. 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 to mention that the presence of HA negatively affect 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).

3.3.4. Influence of temperature on sorption of metalloids on Fe-modified peat

Temperature is one of the factors that certainly affect sorption; therefore, Fe-modified peat was selected as a sorbent to represent the impact of temperature on the sorption process as well as to give the insight data about the sorption mechanism. The impact of temperature on the sorption capacity of metalloids on Fe-modified peat was tested at four temperatures: 275 K, 283 K, 298 K, and 313 K. It was observed that sorption capacity increased with increase of temperature for all of studied metalloids. An example of the impact of temperature on sorption of Sb(V) is shown in Figure 3.12.

Obtained results for sorption of antimony at various temperatures are in agreement with the data reported by J. Xi (2010), where sorption of Sb(V) on kaolinite also increased with rose of temperature. Obtained results can be explained by the fact that higher temperature can cause an increase of diffusion rate by molecules of adsorbate as well as it may affect the pore size of a sorbent or can cause the multiplication of sorption sites by breaking down some of the internal bonds near the edges of particles (Partey *et al.* 2008).

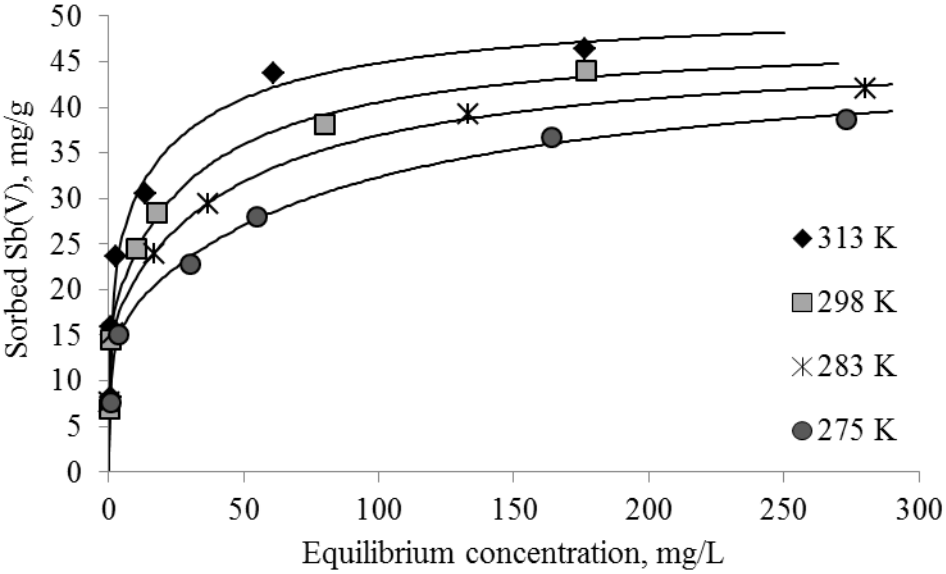

Fig. 3.12 Impact of temperature on sorption of Sb(V) on Fe-modified peat, initial concentration of Sb(V) 100–800 mg/L, sorption time 24 h

The linear Langmuir sorption isotherm form was used to obtain the Langmuir isotherm constant (K) and further calculation of thermodynamic parameters. The Gibbs free energy (ΔG˚), standard enthalpy (ΔH˚), and standard entropy changes (ΔS˚) were calculated using equations. 3.8., 3.9., and 3.10.:

$$\Delta G^{\circ} = -R \cdot T \cdot \ln K, \quad (3.8.)$$

$$\ln\left(\frac{K_1}{K_2}\right) = -\frac{\Delta H^0}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad (3.9.)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\,\Delta S^{\circ}, \quad (3.10.)$$

where K is the Langmuir isotherm constant (L/mol) at temperature T (K) and R is the ideal gas constant (8.314 J/mol K). Calculated Langmuir constants and thermodynamic parameters are given in Tables 3.3 and 3.4.

Negative ΔG˚ values for the sorption of metalloids (Table 3.3) on modified peat indicate that the sorption process of metalloids is of a spontaneous nature and the adsorptive forces are strong enough to break the potential barrier. The fact that the values of ΔG˚ become more negative with increase of temperature refers to more efficient adsorption at a higher temperature.

Positive ΔH˚ values, in turn, indicate to an endothermic nature of sorption of metalloids on modified peat and the process promoted at high temperature. Furthermore, positive values of standard entropy show increase of the degree of freedom of the adsorbed metalloid species onto modified peat. In the case when change of enthalpy is positive and TΔS is negative, favourable is entropic change and thus disorder increases (Al-Anber 2011, Ho and Ofomaja 2005, Partey *et al.* 2008, Xi *et al.* 2010).

Table 3.3

Calculated Langmuir constants and Gibbs free energy for modified peat used as a sorbent

T (K)	K (L/mol)					
	As(III)	As(V)	Sb(III)	Sb(V)	Te(IV)	Te(VI)
275	7692	8997	16552	10000	–	23000
283	7692	–	17960	14150	25000	15600
298	11111	12762	18105	20769	50000	35500
313	12500	13247	18075	32125	80000	57800
T (K)	**ΔG° (kJ/mol)**					
	As(III)	**As(V)**	**Sb(III)**	**Sb(V)**	**Te(IV)**	**Te(VI)**
275	–20.5	–20.8	–22.2	–21.1	–	–22.9
283	–21.9	–	–23.0	–22.5	–23.8	–22.7
298	–22.2	–23.4	–24.3	–24.6	–26.8	–25.9
313	–24.5	–24.7	–25.5	–27.0	–29.4	–28.5

Table 3.4

Calculated standard enthalpy (ΔH˚), and standard entropy changes (ΔS˚) for modified peat used as a sorbent

	ΔH˚ (kJ/mol)	ΔS˚ (J/mol K)
As(V)	7.5	103
As(III)	9.1	107
Sb(V)	21.9	156
Sb(III)	1.3	86
Te(VI)	32.2	195
Te(IV)	28.6	185

In summary, obtained results are in agreement with other studies suggesting that the sorption process of metalloids using different sorbents based on natural materials is spontaneous and endothermic (Partey *et al*. 2008, Xi *et al*. 2010), at the same time it is greatly dependent on the materials used.

3.3.5. Sorption kinetics study of metalloids on Fe-modified peat

Sorption kinetics gives valuable insight in the pathway of sorption process and sorption mechanism. The sorption kinetics of metalloids on Fe-modified peat was studied as a function of time at room temperature.

According to the results of sorption kinetics study, sorbed amount of each metalloid exceeded 55 % after 1 h (Fig. 3.13). Sorbed amount of As(III) exceeded 90 % after 2 h, while 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.

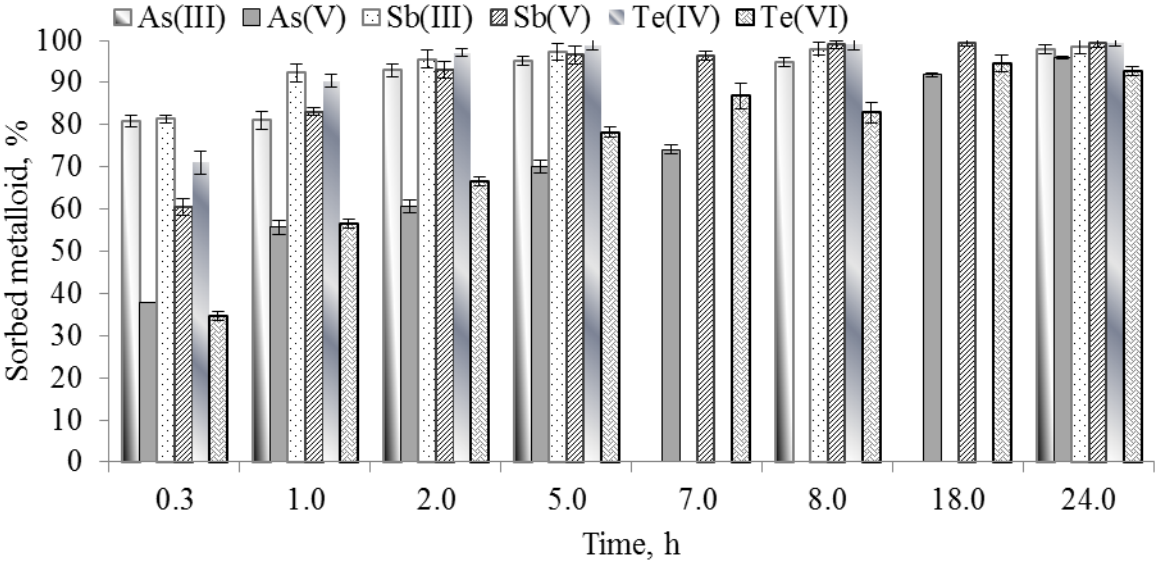

Fig. 3.13 Sorption kinetics study of metalloids on Fe-modified peat, initial concentrations of As and Te is 100 mg/L, Sb – 200 mg/L, at room temperature

In comparison with other studies it was set that a contact time of 48 h is needed to reach the equilibrium using waste metal hydroxide entrapped into 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 (Escudero *et al*. 2009). Sorption experiments of Sb(III) and Sb(V) onto Fe oxides (e.g., goethite) and clays (e.g., bentonite) indicated that sorption process is fast. It is suggested that 24 h is sufficient time to reach sorption equilibrium of Sb(III) and similar tendency is characteristic also for Sb(V) (Xi *et al.* 2011, Xi *et al.* 2013).

Several models are used to describe the model of sorption kinetics process. In order to establish the sorption model, sorption constants were calculated using the pseudo-first and pseudo-second-order equations. Appropriate sorption model was determined comparing the determination coefficients in the pseudo-first and pseudo-second-order equations. In all occasions experimental data fitted the best to the pseudo-second-order kinetic model. 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 (Ho and McKay 2000).

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. (3.11.) (Ho and Ofomaja 2005).

$$q_t = \frac{t}{(1/kq_e^2) + (t/q_e)} \tag{3.11}$$

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

The linear form of Eq. (3.11.) is:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \tag{3.12.}$$

Eq. (3.12.) can be transformed to obtain Eq. (3.13.):

$$\frac{q_t}{t} = \frac{h}{1 + kq_e t} \tag{3.13.}$$

where h = kq_e^2, and h characterises the initial sorption rate as q_t/t, when t→0 (Mohan and Pittman 2007). 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 3.4.

Table 3.4

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

Metalloid	**Sorbed, mg/g**	**k, g/mg min**	**h, mg/g min**
As(III)	7.64	0.0130	0.7606
As(V)	7.94	0.00171	0.1081
Sb(III)	14.33	0.0153	3.1387
Sb(V)	14.84	0.0014	0.2504
Te(IV)	7.51	0.02584	1.4583
Te(VI)	6.59	0.00214	0.0931

Kinetic experiments depending on the temperature indicate that sorbed amount of metalloid is increasing with increase of temperature. Such trend is observed for each form of 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. 3.14.). It is possible to determine sorption activation energy using 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 overcome by the sorbate ion or molecule to interact with functional groups on the surface of the sorbent (Saha and Chowdhury 2011).

$$k_2 = k_0 \cdot e^{\frac{-Ea}{RT}} \tag{3.14.}$$

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

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 $\ln k_0$.

Calculated amount of activation energy for Fe-modified peat sorbing metalloids is given in Table 3.5.

Table 3.5

Calculated activation energy for Fe-modified peat sorbing metalloids

Metalloid	**E_a, kJ/mol**
As(III)	16.96
As(V)	8.06
Sb(III)	8.32
Sb(V)	31.99
Te(IV)	10.79
Te(VI)	7.59

Positive values of activation energy indicate that sorption process is favourable at higher temperatures, thus indicating an endothermic nature of sorption process (Anirudhan and Suchithra 2010).

There is an assumption that low values of activation energy refers to diffusion controlled transport and physical sorption process, whereas higher activation energy refers to chemisorption or surface controlled processes (Ayoob *et al*. 2008). In accordance with other studies, activation energy of 5–40 kJ/mol corresponds to physical sorption, while 40–800 kJ/mol corresponds to chemisorption (Bekçi *et al.* 2009, Chen and Chen 2009, Suteu and Malutah 2013). Wherewith sorption of As(III), As(V), Sb(III), Sb(V), Te(IV) and Te(VI) on Fe-modified peat mainly occur according to mechanisms of physical sorption processes. Since activation energy of As, Te and Sb(III) is lower than 25 kJ/mol and the rate (limiting step of the sorption process) could be controlled by diffusion.

Conclusions

- ✓ Modification of materials with Fe compounds significantly enhance the sorption capacity of the sorbents used for sorption of arsenic, antimony and tellurium.
- ✓ Fe-modified peat is the best sorbent applicable for removal of metalloids (As, Sb, Te). Fe-modified moss and Fe-modified saw dust are sorbents that also can effectively sorb all studied metalloids (As, Sb, Te).
- ✓ Fe-modified straw and Fe-modified reed can be effectively used in areas where concentration of metalloids is relatively low (<10 mg/L).
- ✓ The sorption ability of studied sorbents sorbing As(V) and Sb is affected by pH of a solution. The best sorption conditions are at pH interval 3–6 for removal of As(V) and Sb(V), at pH 6.5–9 for removal of Sb(III), while there is no significant impact of pH on removal of As(III) and both, Te(IV), and Te(VI), at the studied conditions (pH 3–9).
- ✓ Obtained results point to the formation of inner-sphere complexes at the water-solid interface of Fe-modified peat sorbing As(V), Sb(III), Sb(V), Te(IV) and Te(VI), because in all the cases the sorbed amount of metalloids increased with the increase in ionic strength. It is possible that Fe-modified peat sorbing As(III) is forming outer-sphere complexes.
- ✓ Competing ions as well as HA affect sorption of metalloids on Fe-modified peat. Minor impact on the reduction of metalloid sorption was detected at 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. 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 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).
- ✓ Calculated thermodynamic parameters suggest that the sorption process of As(III), As(V), Sb(III), Sb(V), Te(IV) and Te(VI) onto Fe-modified peat is of a spontaneous nature and it is an endothermic reaction. The fact that the values of the Gibbs free energy (ΔG°) become more negative with increase of temperature indicates more efficient sorption at a higher temperature.
- ✓ Sorption of metalloids on Fe-modified peat mainly occurs relying on mechanisms of physical sorption processes.

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