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Biomass sorbents for metalloid removal

Linda Ansone · Maris Klavins · Maruta Jankevica · Arturs Viksna

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Abstract The present work investigates the sorption of metalloids—As(V), Sb(V), and Te(VI)—on Fe-modified biomaterials (Fe-modified peat, shingles, moss, straw, canes, and sand) using batch tests. The said sorption was studied as a function of initial metalloid concentration, pH, and temperature. The highest sorption capacity was observed for Fe-modified peat. Fe-modified moss and Fe-modified shingles can also be used in severely polluted waters. The best sorption conditions are in the pH interval 3–6.5 for As(V) and Sb(V), while pH 3–9 is the most appropriate interval for Te(VI) removal. The impact of temperature on the metalloid sorption capacity of Fe-modified peat was tested at four temperatures: 275, 283, 298, and 313 K, and the sorption capacity increased with increase in temperature for all of the studied metalloids. The calculated thermodynamic parameters suggest that the sorption process is of a spontaneous nature and endothermic.

Keywords Biomass sorbents · Arsenic · Antimony · Tellurium · Sorption

L. Ansone (✉) · M. Klavins · M. Jankevica
Department of Environmental Science, University of Latvia,
Raina Blvd 19, Riga 1586, Latvia
e-mail: linda_ansone@inbox.lv

M. Klavins
e-mail: maris.klavins@lu.lv

M. Jankevica
e-mail: maruta.jankevica@gmail.com

A. Viksna
Faculty of Chemistry, University of Latvia, Raina Blvd 19,
Riga 1586, Latvia
e-mail: arturs.viksna@lu.lv

1 Introduction

Recently, growing attention is being paid to environmental pollution with metalloids (As, Sb, Te) (Ansari and Sadegh 2007; Nemade et al. 2009; Ko et al. 2004; Filella et al. 2002; Ceriotti and Amarasiriwardena 2009; Zhang et al. 2010). Due to the wide distribution and toxicity, arsenic is the most studied metalloid. At the same time, considerably less attention has been given to antimony and tellurium. However, it is important to study the occurrence of antimony and tellurium in the environment, associated environmental pollution and possible solutions for environmental remediation.

Arsenic is a naturally occurring element that ranks 20th in natural abundance (Mohan and Pittman 2007). Since prehistoric times, arsenic constantly has been in the centre of attention. Arsenic is mobilized in natural water systems through the range of anthropogenic as well as natural sources. For example, geochemical interactions that occur between arsenic-containing rocks and minerals and water, biological activity and volcanic emission, as well as soil erosion and leaching are some of 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 arsenic insecticides, herbicides and crop desiccants, as well as the use of arsenic additives to livestock feed (Henke 2009; Anirudhan and Unnithan 2007; 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 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 redox conditions (Ansari and Sadegh 2007, Pokhrel and Viraraghavan 2006). In the pH range 3–9, the dominant species of As(III) is the neutral H_3AsO_3, while those of As(V) are the negatively charged $HAsO_4^{2-}$ and $H_2AsO_4^{-}$ (Nemade et al. 2009; Ko et al. 2004).

Arsenic distribution, 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 involve skin, lung, bladder and kidney cancers, pigmentation changes, 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, United States, and Europe (Klemm et al. 2005; Moller et al. 2009; Smedley and Kinniburgh 2002). Furthermore, drinking water supplies in polluted areas contain dissolved arsenic in quantities more than 10 µg/L, which is the threshold value recommended by the World Health Organization that many nations have adopted as their regulatory standard (Henke 2009; Dupont et al. 2007).

Antimony, like arsenic, is present in the environment as a result of natural and human activities. Natural antimony sources include rock weathering, soil runoff, as well as geothermal waters. The antimony concentration in unpolluted waters is low—most frequently less than 1 µg/L, while in polluted areas—close to anthropogenic sources—the concentration can be up to 100 times higher in comparison to natural levels (Filella et al. 2002).

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

Similarly to arsenic, antimony can exist in a variety of oxidation states: −3, 0, +3, and +5, while mainly it occurs in inorganic forms—Sb(III) and Sb(V)—in the environment, although, as a result of soil microbial activities, the organic forms of antimony, for example, trimethyl antimony ($(CH_3)_3Sb$), can also been produced (Ceriotti and Amarasiriwardena 2009). Like arsenic(V), Sb(V) is the predominant species in oxic systems and Sb(III)—in anoxic systems, although significant amounts of Sb(III) and Sb(V) have been found in oxic and anoxic systems respectively. The reasons of these occurrences could be biological activity or kinetic effects (Steely et al. 2007; Filella et al. 2002). It is suggested that $Sb(OH)_6^-$ is the predominant form of antimony in aqueous environment in the pH range 2–11 (Sun 2011; Xi et al. 2011).

Like arsenic, 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, as recommended by EU (Council of the European Union 1998). Antimony, like arsenic, is toxic, and trivalent species are reported to be more toxic than pentavalent species (Filella et al. 2002; Ceriotti and Amarasiriwardena 2009). The solubility of antimony compounds in biofluids, Sb valence state and presence of complexing agents affects the Sb toxicity (Ceriotti and Amarasiriwardena 2009; Steely et al. 2007). It is suggested that in the human body, antimony may interact with –SH groups in cellular components, particularly with enzymes, thus inhibiting the enzymatic activity. Therefore, a toxic effect of Sb in high doses is observed (Ceriotti and Amarasiriwardena 2009).

Although tellurium is found in low abundances in the Earth crust, its toxicity can induce local environmental problems. Up to now, there have not been many studies on tellurium and its compounds in the environment, and the main attention in the existing studies has been focused on tellurium pollution near main tailing 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 to steel and copper to provide machinability (Wang et al. 2011; Zhang et al. 2010).

Tellurium can exist in four oxidation states (−II, 0, IV and VI) 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 in the pH range 7.5–11, while H_6TeO_6 is the predominant form at pH <7.7 (Hein et al. 2003; Schweitzer and Pesterfield 2009). Like it is 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 be accumulated in kidneys, heart, liver, and spleen, and if its content exceeds 0.002 g/kg, kidney and liver degeneration can be induced (Zhang et al. 2010).

Many technologies for the removal of metalloids from aqueous systems have been developed, for instance, oxidation, coagulation, precipitation with iron, manganese and aluminium oxy(hydr)oxides, ion exchange, adsorption, and reverse osmosis (Anirudhan and Unnithan 2007; Parga et al. 2009; Xi et al. 2010; Uluozlu et al. 2010). 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 economical and easy to set up (Dupont et al. 2007; Zhang and Itoh 2005; Uluozlu et al. 2010).

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. Recently, great attention has been paid to the sorbents based on natural materials. 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. On this account, metalloid removal using new Fe-modified sorbents based on common natural materials were investigated in this study.

2 Experimental part

Analytical quality reagents (Merck Co., Sigma-Aldrich Co., Fluka Chemie AG RdH Laborchemikalien GmbH Co.) were used without further purification. For the preparation of solutions, high purity water Millipore Elix 3 (Millipore Co.) 10–15 MΩ cm was used throughout.

Sodium arsenate heptahydrate ($Na_2HAsO_4{\cdot}7H_2O$ from Sigma-Aldrich), potassium hexahydroxoantimonate (V) ($KSb(OH)_6$ from Fluka), and telluric acid (H_6TeO_6 from Aldrich) were analytical grade chemicals. Peat was obtained from Gagu Bog (Latvia) and modified chemically.

2.1 Methods of synthesis

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

2.2 Characterization 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 moisture content, organic substances content, and Fe_2O_3 analysis.

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 program. Samples were pressed in KBr pellets, and the spectra were recorded in the range of 4,000–400 cm^{-1} with a 4 cm^{-1} resolution.

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

The surface area was measured using a surface area pore size analyser Gemini2360. The BET method was used for the specific surface area measurements.

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

$$LOI_{550} = \frac{DW_{105} - DW_{550}}{DW_{105}} \cdot 100$$

where LOI_{550} represents LOI at 550 °C (as a percentage), DW_{105} represents the dry weight of the sample before combustion, and DW_{550}—the dry weight of the sample after heating to 550 °C.

The Fe_2O_3 content was determined in samples after heating at 550 °C. Samples were mineralized using concentrated HCl and conc. HNO_3 and heated at 120 °C for 2 h. Fe in the corresponding filtrates after dilution was analysed using an atomic absorption spectrometer with flame atomization (FAAS) (Perkin-Elmer Analyst 200 atomic absorption spectrophotometer).

2.3 Sorption experiments

Sorption experiments were conducted using a batch system. $Na_2HAsO_4{\cdot}7H_2O$ was used for As stock solution preparation at a concentrations from 5 to 300 mg/L;

$KSb(OH)_6$ and H_6TeO_6 were used for Sb and Te stock solution preparation accordingly (10–800 mg/L). 40 mL of metalloid solution was added in each 100 mL glass vessel with 0.5 g sorbent. Vessels were shaken for 24 h at the room temperature. Suspension was then filtered, and arsenic in the filtrate was analysed using a Perkin-Elmer atomic absorption spectrophotometer AAnalyst 600 with graphite furnace (ETAAS—Electrothermal Atomic Absorption Spectrometry). Antimony and tellurium were analysed using the atomic absorption spectrophotometer PerkinElmer AAnalyst 200 with flame atomisation (FAAS).

To investigate the impact of temperature on metalloid removal, sorption experiments were carried out at 275, 283, 298 and 313 K. Sorbent/sorbate ratio was kept as previously mentioned.

To investigate the pH impact, 0.1 M NaOH and 0.1 M HCl were used. In glass vessels, to the 0.5 g of peat the necessary amount of arsenic, antimony or tellurium stock solution was added, then the varied pH solutions were prepared by adding 0.1 M NaOH or 0.1 M HCl dropwise to achieve pH values of 3 through 10, after that the reaction mixture was shaken for 24 h at the room temperature and filtered, and finally the pH scale was measured. The initial concentration of arsenic and tellurium used for the solution was 100 mg L^{-1}, and the initial concentration of antimony was 200 mg/L. The filtrates were analysed with FAAS or ETAAS.

3 Results and discussion

3.1 Characterization of sorbents

FT-IR spectra, SEM images, nitrogen adsorption isotherm measurements, as well as moisture content, organic substances content, and Fe_2O_3 analyses were used to characterize the obtained sorbents.

The surface morphology of the sorbents used slightly differs (Fig. 1). Decomposed plant residues are characteristic of the raw peat material (Fig. 1a), and differences of surface morphology between raw and modified peat are manifest when comparing images a and b in Fig. 1. The plant residues coated with iron compounds are characteristic of the modified peat. The surface morphologies of modified shingles, modified canes and modified moss are shown in images c, d, and e of Fig. 1. SEM images of Fe-modified biomaterials are similar to the surface morphology of Fe-modified peat, thus indicating similar source materials.

The content of organic matter for all analysed sorbents of an organic origin are similar and varies from 74 to 83 %. As it was expected, Fe-modified sand shows a considerably lower content of organic substances in comparison to other Fe-modified sorbents (Table 1). 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 compared to other Fe-modified sorbents used in this study (Table 1). So, the specific surface area is one of the most important parameters that affect sorption and, taking into account the high affinity between metalloids and iron compounds, one can predict that the sorbents with the highest specific surface area and the highest iron oxide content will have the highest sorption capacity. In this case, modified peat has the relevant properties that could ensure a high sorption capacity and thus can be effective for metalloid removal.

FT-IR spectrometry is one of the methods that are used to characterise sorbent materials, as it provides for an opportunity of establishing main functional groups that are present in a sorbent as well as noticing structural differences in comparing unmodified and modified materials.

Comparing the FT-IR spectra of Fe-modified and raw materials (peat, shingles, straw, moss and canes) (Fig. 2), the main differences are observed at the wavenumber interval 1,700–450 cm^{-1}, whereas the common features for all the FT-IR spectra of the sorbent materials investigated in this study are as follows: a broad band at 3,600–3,300 cm^{-1}, which corresponds to hydroxyl groups in phenols and carboxylic acids; the FT-IR signal at 1,430 cm^{-1}, which characterises the methyl C–H asymmetric/symmetric bends; and the aromatic C–H bend signal observed at the 1,225–950 cm^{-1} interval (Coates 2000).

The intensity of several functional group signals varies in comparing modified and unmodified materials, thus indicating the formation of Fe complexes and corresponding structural changes in molecules that have occurred due to interaction with metals. FT-IR spectra normalization was done using program Spectrum v 5.3.1 and relation of band intensities at 1,700 and 1,600 cm^{-1} were used to compare appropriate signals of functional groups before and after material modification. The obtained results are in agreement with previous studies, for example, in the report of Rodriguez-Lucena et al. (2009), it is said that the bands at 2940, 2830, 1715, 1470, 1500, and 1050 cm^{-1} are less intense after the formation of complexes with iron compounds. The lower intensity of separate bands may be related to the formation of Fe phenolates and carboxylates. Such bands could be –CH, –C=O (carbonyl) and –COOH stretching, CH deformation, aromatic ring vibrations, C=C aromatic skeletal vibrations, and C–O, C–C and C–OH vibrations (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 the metalloid sorption on unmodified materials (peat, straw, shingles, moss, and

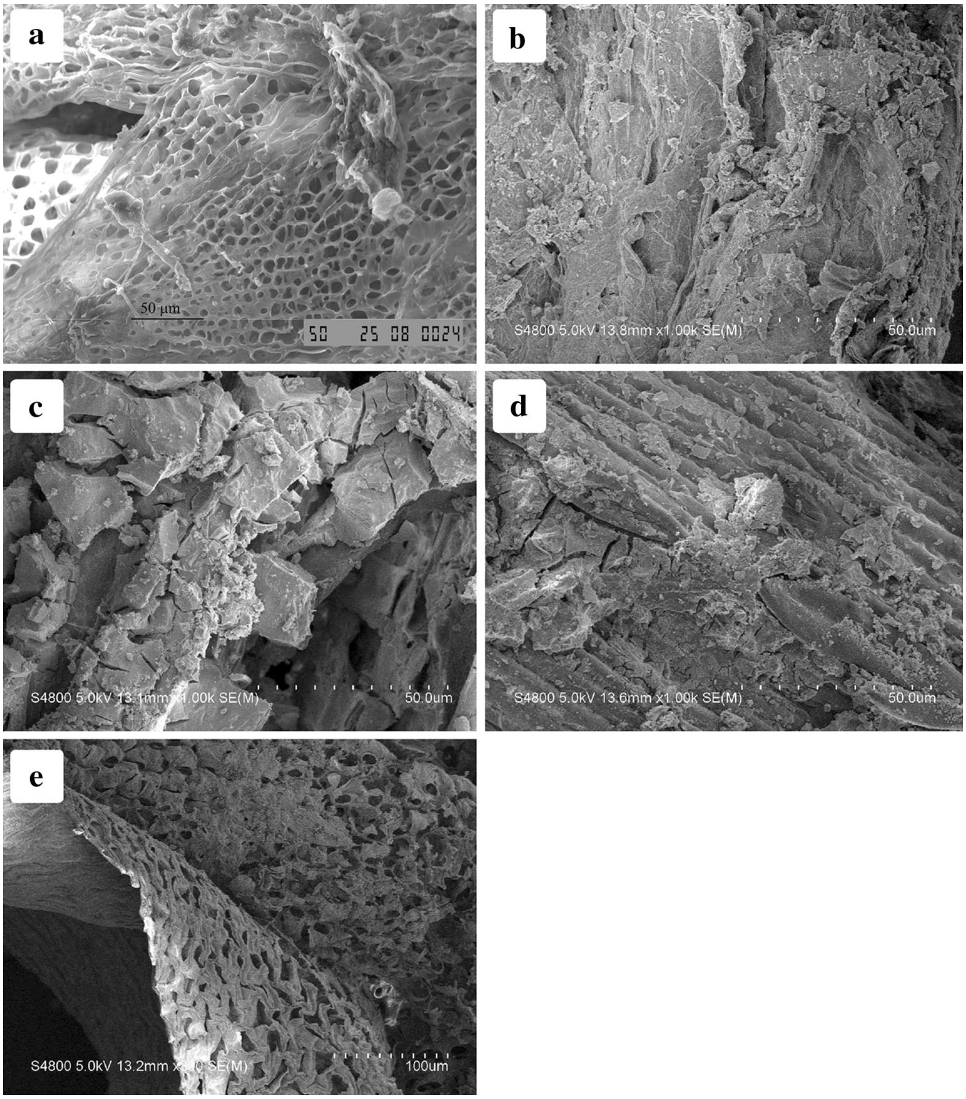


Fig. 1 SEM image of **a** raw peat material, **b** modified peat, **c** modified shingles, **d** modified canes, **e** modified moss

Table 1 Characterization of sorbents

Sorbent	LOI (%)	Fe_2O_3 (mg/g)	Specific surface area (BET method) (m^2/g)
Mod. peat	74	424.8	44.16
Mod. shingles	83	297.7	45.31
Mod. canes	79	274.8	40.31
Mod. moss	80	256.5	19.14
Mod. straw	81	292.3	–
Mod. sand	1.2	49.4	–

canes), while the As–O–Fe bond could support interaction between metalloids and Fe-modified biomaterials (mod. peat, mod. shingles, etc.).

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

3.2 Metalloid removal

Sorption isotherms characterise the equilibrium partitioning between sorbed and desorbed phases, providing information about the sorption process. Biosorption has been demonstrated to be a useful alternative to the conventional treatment methods for the removal of metals and metalloids, as well as other pollutants from aqueous solution. Biomaterials are usually pre-treated and modified in order to enhance their sorption capacity. A wide variety of different materials are used to remove metalloids from water with various efficiencies. In this study, sorption experiments were carried out using unmodified materials as well as iron-modified biomass sorbents. To make sure that equilibrium was reached, a time of 24 h was used for

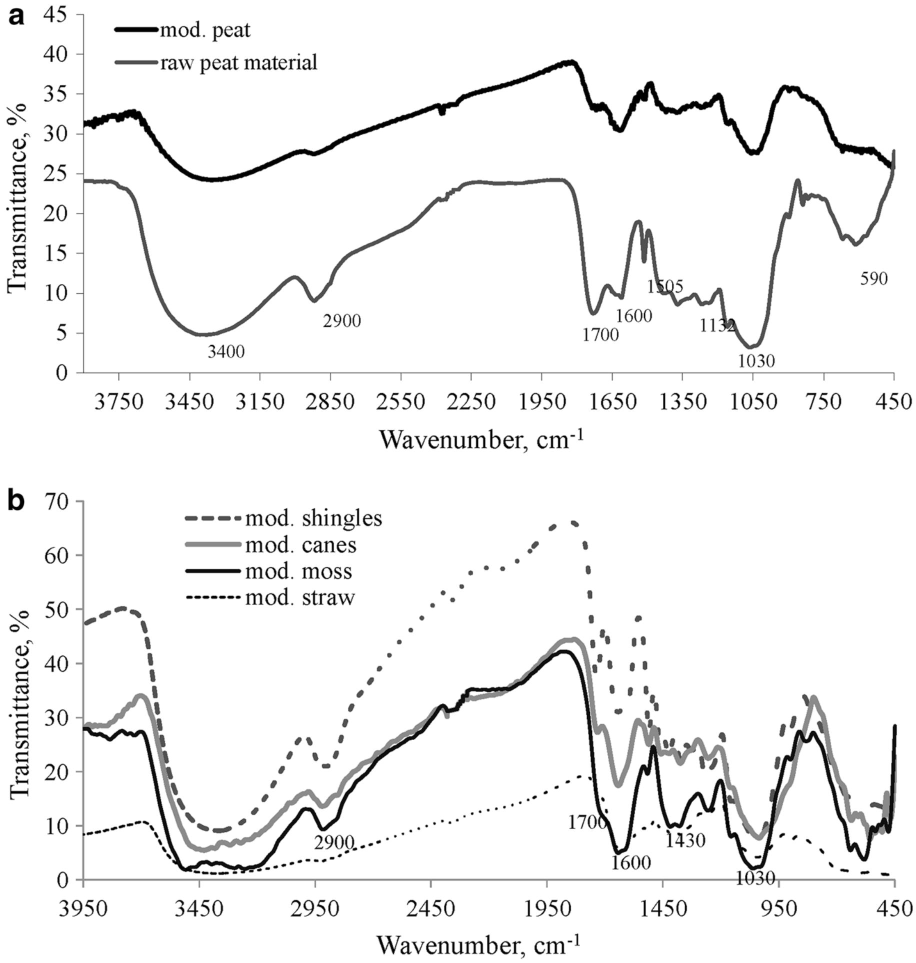


Fig. 2 The FT-IR spectra of **a** Fe-modified peat and raw peat material; **b** Fe-modified biomaterials

sorption tests. The obtained sorption data were correlated using the Langmuir and Freundlich isotherm models. Based on correlation coefficients, the sorption of arsenic(V), tellurium(VI) and antimony(V) using Fe-modified biomaterials as sorbents better fitted to the Langmuir isotherm model, with the exception of the sorption of Sb(V) using Fe-modified moss as a sorbent that better fitted to the Freundlich model.

Metalloid (As(V), Sb(V) and Te(VI)) sorption capacity is dependent on the biomass sorbent used, although reaction conditions for material modification with Fe compounds were similar.

The highest sorption capacity of As(V) was observed for the Fe-modified peat (peat from Gagu Bog) sorbent, whereas Fe-modified moss, Fe-modified shingles and Fe-modified straw showed similar but not so high results. The sorption capacities of Fe-modified sand and Fe-modified canes were less than 2 mg/g (Fig. 3). Fe modified biomaterial sorbent synthesis was based on method of modified polymeric/inorganic hybrid sorbent suggested by DeMarco et al. (2003). We suggest that Fe oxyhydroxide containing particles reside within the pores of peat and they could be easily accessible to arsenates and arsenites as well as other used forms of metalloids. It is possible that protonated as well as electrically neutral iron oxides selectively sorb arsenic species through formation of inner sphere complexes.

Unmodified natural materials, such as raw peat material, are not useful for arsenic(V) removal, although their impregnation with Fe compounds significantly enhance the sorption capacity, as seen in Fig. 1 if we compare the sorption isotherms of raw peat material and Fe-modified peat.

For a better understanding, the sorbed amounts of arsenic at corresponding sorbate/sorbent ratios and experimental conditions were calculated to percentage. Iron-modified peat can sorb 98 % at the initial concentration of 100 mg/L, and the sorbed amount of arsenic decreases to 70 % if the initial arsenic concentration reaches 270 mg/L. The sorbed amounts of modified shingles, modified moss and modified straw exceed 95, 97 and 99 % accordingly if the initial arsenic concentration is 45 mg/L, whereas less effective sorbents, such as modified canes and modified sand, can be used effectively at lower arsenic concentrations. Fe-modified canes sorb more than 97 % of As(V) if the initial concentration of arsenic does not exceed 40 mg/L,

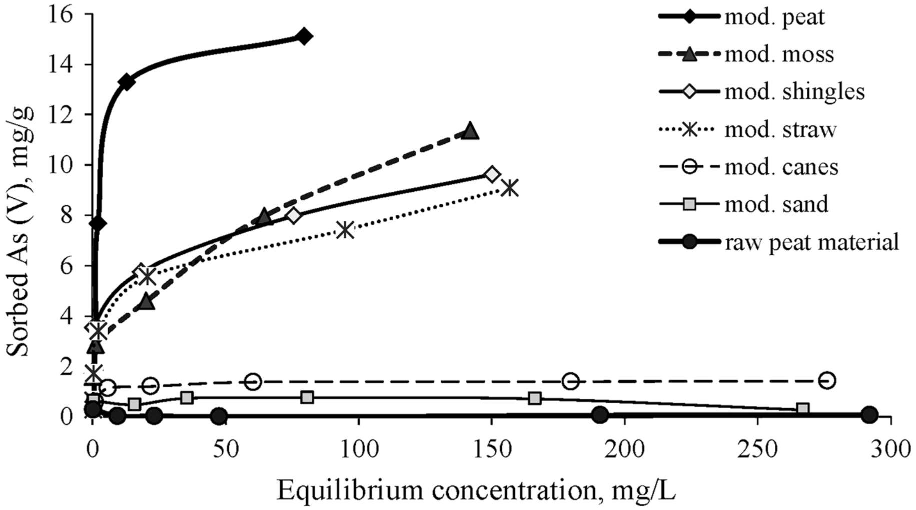


Fig. 3 Arsenic removal using iron-modified biomass, sorption time 24 h, room temperature

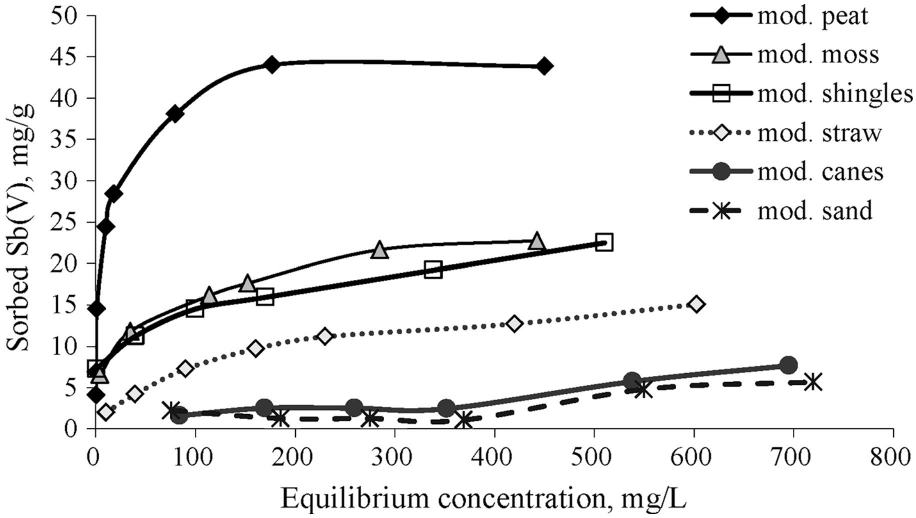


Fig. 4 Antimony removal using iron-modified biomass, sorption time 24 h, room temperature

and modified sand can sorb 94 % if the initial arsenic concentration does not exceed 10 mg/L.

To summarise, iron-modified peat was the most effective sorbent for arsenic removal, and it is possible to use this sorbent for waters severely polluted with arsenic. We also propose that Fe-modified moss, Fe-modified shingles and Fe-modified straw can be applied in areas where arsenic concentration is lower.

In comparison to arsenic, antimony(V) removal using Fe-modified biosorbents is considerably higher (Fig. 4). The sorption capacity of Fe-modified peat exceeds 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 concentration of 370 mg/L, and it decreases to 75 % at the initial concentration of 730 mg/L. Fe-modified peat is the best sorbent for both As and Sb, as shown in Figs. 3 and 4. The properties for the removal also might be related to the fact that peat is rich in organic substances with diverse properties, but dominant functional groups are carboxylgroups and phenolic hydroxyls. Minor importance has amino groups, but also they might contribute to arsenic sorption. Peat organic matter has hydrophobic structures, possibly contributing to sorption of arseno-organic species. Thus, based on literature studies and FT-IR spectra, we suggest that iron is chemically bonded, but the sorption is a joint effect of peat organic structural units and iron oxo(hydroxides). In addition, further experiments that would prove that are planned.

Fe-modified moss as well as Fe-modified shingles shows a similar sorption capacity, although the results are not as high as using Fe-modified peat. The sorbed amount of modified moss and modified shingles exceed 95 % at the initial concentration of 90 mg/L, and it decreases to 48 and 41 % at initial concentrations of 556 and 580 mg/L for modified moss and modified shingles accordingly. Fe-modified straw can be used in less polluted areas. Modified straw can sorb up to 57 % of Sb(V) if the initial antimony concentration is 92 mg/L, but then, like it was in the case of arsenic, Fe-modified canes and Fe-modified sand are less

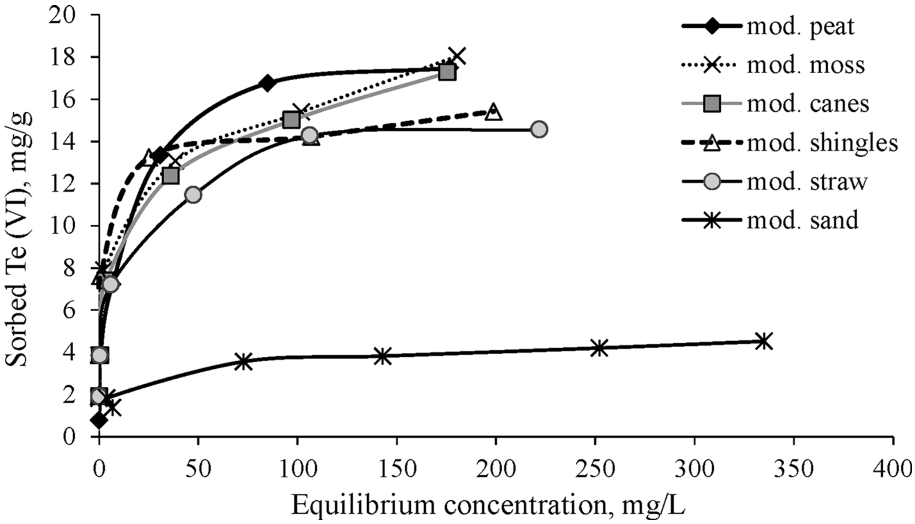


Fig. 5 Tellurium removal using iron-modified biomass, sorption time 24 h, room temperature

effective sorbents, although the sorption capacities of modified canes and modified sand are greater for antimony than for arsenic.

To sum up, the biosorbents used in this study are very effective in removing antimony. Although As(V) and Sb(V) have similar chemical properties, the sorption capacity of modified peat and other sorbents used in this study is almost 3 times higher compared to Sb(V) and As(V).

Comparing the sorption isotherms of As(V) (Fig. 3) and Sb(V) (Fig. 4), it is well seen that Fe-modified peat has a noticeably higher sorption capacity than other Fe-modified sorbents, while the result is quite different in the case of tellurium removal (Fig. 5). These differences could be due to different sorbate structures and corresponding chemical properties. The 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 canes can sorb about 55 % of Te at the initial Te concentration of 400 mg/L, and if the initial concentration of Te(VI) decreases to 100 mg/L, the sorbed Te(VI) amount reaches more than 90 %. A similar trend was observed also for Fe-modified shingles and Fe-modified straw that can sorb about 47 % at the initial concentration of 400 mg/L, while the sorbed amount increases to 95 and 93 % accordingly if the initial Te(VI) concentration is 100 mg/L. Fe-modified sand was the least effective sorbent for Te(VI) in comparison to other sorbents used in this study. It can sorb up to 70 % at the initial concentration of 25 mg/L.

To sum up, Fe-modified peat, modified moss and modified canes can be used as sorbents for waters severely polluted with tellurium, and the other sorbents can be used when the tellurium concentration is lower.

In conclusion, the obtained results correspond to the previously accepted hypothesis that modified peat could have a higher sorption capacity due to its higher specific surface area and iron oxide content. Comparing the arsenic, antimony and tellurium sorption capacities using unmodified and modified biomaterial sorbents, it is obvious that the sorption capacities have significantly increased after modification. It can be inferred from both the study of literature and the obtained results that the reason of such an outcome could be the formation of a metalloid-O–Fe bond in Fe-modified sorbents (for example, As–O–Fe, Sb–O–Fe). This assumption has also been confirmed by other studies. For example, Dupont et al. (2007) suggest that the solid phases loaded with Fe species can sorb arsenates, possibly due to the formation of stable inner and outer sphere surface complexes as a result of the interaction between As_2O_3 or AsO_4 with FeO_6 polyhedra (Dupont et al. 2007). There is also evidence for complex formation between arsenic oxyanions and the ferric iron complexes of humic substances (HSs). A spectroscopic evidence for ternary complex formation between the As(V) and Fe(III)–HS complexes was given by Mikutta and Kretzschmar (2011) using EXAFS. Moreover, an EXAFS study on the speciation of Sb(V) on goethite confirms that the $Sb(OH)_6$ octahedron forms an inner-sphere edge-sharing adsorption complex with the $Fe(OH)_6$ octahedron, suggesting a bidentate interaction (McComb et al. 2007), whereas Harada and Takahashi (2009) confirm the formation of inner-sphere complexes as a result of interaction between Te(VI) and Fe(III) hydroxide.

The sorption capacities of the sorbents synthesised in this study are comparable with those of other biomaterials. For example, the study of Thirunavukkarasu et al. (2001) found that the sorption capacity of Fe oxide-coated sand and ferrihydrite used for arsenic removal from natural water was 18.3 and 285 µg/g respectively, and a comparatively high sorption capacity of As (V) was obtained using modified biomasses (*P. chrysogenum*): 37.85 mg/g for HDTMA-Br-modified Mycan biomass, 56.07 mg/g for Magnafloc-modified biomass, and 33.31 mg/g for Dodecylamine-modified biomass (Loukidou et al. 2003). Xi et al. (2010) reported that the sorption capacity of kaolinite used for Sb(V) sorption was 59 µg/g at 298 K. Although there have been some Te(IV) sorption experiments using nano TiO_2 (Zhang et al. 2010), studies on the sorption of Te(VI) are for the most part scanty. However, there is no question that the conditions—such as the amount of sorbent used, metalloid concentration, pH, and others—are crucial, as they noticeably influence the sorption capacity. At the same time, these differing conditions complicate comparing the efficiency of different sorbents.

The effect of pH is one of the most important factors that influence sorption. The pH influence on the sorption process of arsenic(V), antimony(V) and tellurium(VI) was also investigated in this study. The interval of pH (3–9) was chosen to be comparable with possible environmental conditions. The inorganic arsenate species is negatively charged in the pH range 3–9. For As(V), the corresponding stable species and pH values are 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).

Sorption capacity of Fe-modified peat sorbing As(V) and Sb(V) is maximal at acidic pH values and much lower at basic pH values. As it is seen from Fig. 6, the best sorption conditions are in the pH interval 3–6.5 for As(V), when $H_2AsO_4^-$ is the predominant form in the solution. Similar trend was observed also for Sb(V), where negatively charged $Sb(OH)_6^-$ is the predominant form. pH has not significant impact on tellurium removal at the studied conditions. For the purpose of interpretation of the obtained data, it could be supposed that the sorption of As(V), Sb(V), as well as Te(VI) onto Fe-modified biosorbents mainly occurs depending on the interaction between the ionic species of the respective element and the charged surface groups of the sorbent. As it has been suggested in earlier studies, it is possible that sorption occurs by means of a reaction between the positively charged surface groups of $FeOH_2^+$ and negatively charged arsenate (Dupont et al. 2007; Payne and Abdel-Fattah 2005), antimonate or tellurate ions, leading to the formation of surface complexes. Our results are in agreement with other studies, investigating pH influence on arsenate removal using different iron oxides. For example, Mamindy-Pajany et al. suggest that sorption of arsenic using hematite and goethite as sorbents is maximum at acidic pH values (pH 2–7), but negligible at basic pH values (pH 7–12) (Mamindy-Pajany et al. 2009).

Temperature is one of the factors that affect sorption; therefore, Fe-modified peat was selected as a sorbent representing the impact of temperature on the sorption process as well as giving insight into the sorption mechanism. The impact of temperature on the metalloid sorption capacity of Fe-modified peat was tested at four temperatures: 275, 283, 298, and 313 K. The sorption capacity increased with increase in temperature for all of the studied metalloids. An example of the impact of temperature on Sb(V) sorption is shown in Fig. 7. The obtained results of antimony sorption at various temperatures are in agreement with the data reported by Xi et al. (2010), where the sorption of Sb(V) on kaolinite also increases with rise in temperature. The obtained results can be explained by the facts that higher temperatures could cause an increase in diffusion rate by adsorbate molecules as well as make changes in the sorbent pore size or cause the multiplication of sorption sites by breaking down some of the internal bonds near the edges of particles (Partey et al. 2008).

The linear Langmuir sorption isotherm form was used for obtaining the Langmuir isotherm constant (K_a) and further calculation of thermodynamic parameters.

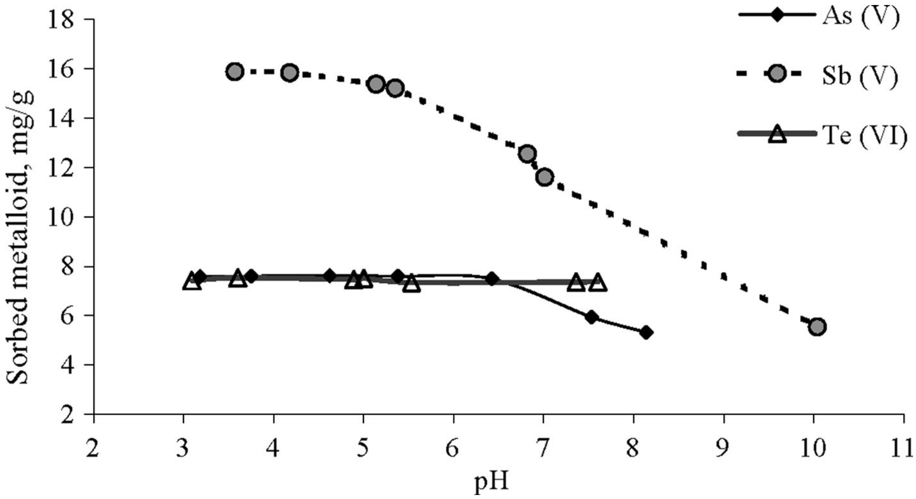
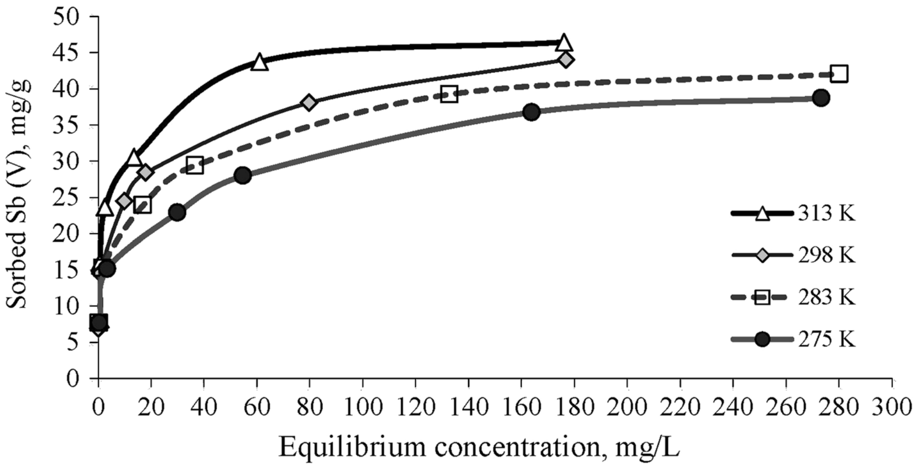


Fig. 6 pH influence on metalloid removal using Fe-modified peat as sorbent, sorption time 24 h, room temperature (As (V) and Te (VI) initial concentration 100 mg/L, Sb (V)—200 mg/L)

Fig. 7 Temperature impact on Antimony (V) sorption on Fe-modified peat, sorption time 24 h



The Gibbs free energy (ΔG°), standard enthalpy (ΔH°), and standard entropy changes (ΔS°) are calculated using Eqs. 1, 2, and 3:

$$\Delta G^{\circ} = -\mathrm{R} \cdot \mathrm{T} \cdot \ln \mathrm{K_a} \tag{1}$$

$$\ln\left(\frac{K_{a1}}{K_{a2}}\right) = -\frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \tag{2}$$

$$\Delta \mathrm{G}^{\circ} = \Delta \mathrm{H}^{\circ} - \mathrm{T}\Delta \mathrm{S}^{\circ}, \tag{3}$$

where $\mathrm{K_a}$ is the Langmuir isotherm constant (L/mol) at temperature T (K) and R is the ideal gas constant (8.314 J/mol K). The calculated Langmuir constants and thermodynamic parameters are given in Tables 2 and 3.

The negative ΔG° values for the sorption of As(V), Sb(V) and Te(VI) (Table 2) onto modified peat indicate that the metalloid sorption process 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 in temperature indicates more efficient adsorption at a higher temperature.

Positive ΔH° values, in turn, indicate that the endothermic nature of metalloid sorption onto modified peat and the process favoured at high temperature. Furthermore, the positive values of standard entropy show increasing the degree of freedom of the adsorbed metalloid species onto modified peat. In the case when enthalpy change is positive and −TΔS is negative, favorable is entropic change and thus disorder increases (Partey et al. 2008; Ho and Ofomaja 2005; Xi et al. 2010; Al-Anber 2011).

To sum up, the obtained results are in agreement with other studies, suggesting that the metalloid sorption process using different sorbents based on natural materials is spontaneous and endothermic (Xi et al. 2010; Partey et al. 2008), at the same time being greatly dependent on the materials used.

Table 2 The calculated Langmuir constants and Gibbs free energy (sorbent—modified peat)

T (K)	K (L/mol)			ΔG (kJ/mol)		
	As(V)	Sb(V)	Te(VI)	As(V)	Sb(V)	Te(VI)
275	4802.0	10,000	23,000	−19.4	−21.06	−22.96
283	4628.1	14,150	15,600	−19.9	−22.49	−22.72
298	8838.2	20769.2	35,500	−22.5	−24.63	−25.96
313	43331.9	32,125	57,800	−27.8	−27.00	−28.53

Table 3 The calculated thermodynamic parameters (sorbent—modified peat)

	ΔH (kJ/mol)	ΔS (J/mol K)
As(V)	41.43	214
Sb(V)	21.98	156
Te(VI)	32.15	195

4 Conclusions

Modification of materials with Fe compounds significantly enhanced the sorption capacities of the sorbents used for sorbing arsenic, antimony, and tellurium. The reason of such an outcome could be a metalloid-O–Fe (for example, As–O–Fe, Sb–O–Fe) bond forming in Fe-modified sorbents. Fe-modified peat is the best sorbent for As(V), Sb(V), and Te(VI). While the sorption capacities for arsenic and tellurium are similar, it is much higher for antimony. Fe-modified moss and Fe-modified shingles are the sorbents used in this study that can effectively sorb all the studied metalloids (As, Sb, Te), although other sorbents, like Fe-modified straw and Fe-modified canes, can also be used in areas where metalloid concentrations are low.

The sorption capacities of the sorbents synthesized in this study are comparable with those of other biomaterials.

However, the conditions—such as the amount of sorbent used, metalloid concentration, pH, and others—are crucial and should be taken into account, as they noticeably influence the sorption capacity and also complicate comparing the efficiency of different sorbents.

The best sorption conditions are in the pH interval 3–6.5 for removal of As(V) and Sb(V), while the pH has not significant impact on tellurium removal at the studied conditions. It can be supposed that the studied metalloid sorption onto Fe-modified biosorbents mainly occurs depending on interaction between the ionic species of the respective element and the charged surface groups of the sorbent.

The impact of temperature on the metalloid sorption capacity of Fe-modified peat was tested at four temperatures: 275, 283, 298, and 313 K, and the sorption capacity increased with increase in temperature for all of the studied metalloids. The calculated thermodynamic parameters suggest that the sorption process is of a spontaneous nature and endothermic. The fact that the values of $\Delta G°$ become more negative with increase in temperature indicates more efficient adsorption at a higher temperature.

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References

Al-Anber, A.M.: Thermodynamics approach in the adsorption of heavy metals, thermodynamics: interaction studies—solids, liquids and gases. In: Moreno-Piraján, J.C. (ed.) (2011)

Anirudhan, T.S., Unnithan, M.R.: Arsenic(V) removal from aqueous solutions using an anion exchanger from coconut coir pith and its recovery. Chemosphere **66**, 60–66 (2007)

Ansari, R., Sadegh, M.: Application of activated carbon for removal of arsenic ions from aqueous solutions. E-J. Chem. **4**(1), 103–108 (2007)

Ceriotti, G., Amarasiriwardena, D.: A study of antimony complexed to soil-derived humic acids and inorganic antimony species along a Massachusetts highway. Microchem. J. **91**, 85–93 (2009)

Coates, J.: Interpretation of infrared spectra, a practical approach. In: Meyers, R.A. (ed.) Encyclopedia of Analytical Chemistry, pp. 10815–10837. John Wiley and Sons, Chichester (2000)

Council of the European Union: Council Directive 98/83/EC on the quality of water intended for human consumption. Adopted by the Council, on 3 November 1998. http://www.lenntech.com/applications/drinking/standards/eu-s-drinking-water-standards.htm#ixzz2HMxCY4bF (1998). Accessed 15 April 2013

DeMarco, M.J., SenGupta, A.K., Greenleaf, J.E.: Arsenic removal using polymeric/inorganic hybrid sorbent. Water Res. **37**, 164–176 (2003)

Dupont, L., Jolly, G., Aplincourt, M.: Arsenic adsorption on lignocellulosic substrate loaded with ferric ion. Environ. Chem. Lett. **5**(3), 125–129 (2007)

Filella, M., Belzile, N., Chen, Y.: Antimony in the environment: a review focused on natural waters I. Occur. Earth-Sci. Rev. **57**, 125–176 (2002)

Guo, H., Stuben, D., Berner, Z.: Arsenic removal from water using natural iron mineral: quartz sand columns. Sci. Total Environ. **377**, 142–151 (2007)

Harada, T., Takahashi, Y.: Origin of the difference in the distribution behavior of tellurium and selenium in a soil–water system. Geochim. Cosmochim. Acta **72**, 1281–1294 (2009)

Hein, J.R., Koschinsky, A., Halliday, A.N.: Global occurrence of tellurium-rich ferromanganese crusts and a model for the enrichment of tellurium. Geochim. Cosmochim. Acta **67**(6), 1117–1127 (2003)

Heiri, O., Lotter, A.F., Lemcke, G.: Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. J. Paleolimnol. **25**(1), 101–110 (2001)

Henke, K.R. (ed.): Arsenic: Environmental Chemistry, Health Threats, and Waste Treatment. Wiley, Wiltshire (2009)

Ho, Y., Ofomaja, A.E.: Kinetics and thermodynamics of lead ion sorption on palm kernel fibre from aqueous solution. Process Biochem. **40**, 3455–3461 (2005)

Jain, C.K., Ali, I.: Arsenic: occurrence, toxicity and speciation techniques. Water Res. **34**(17), 4304–4312 (2000)

Klemm, W., Greif, A., Broekaert, J.A.C., Siemens, V., Junge, F.W., Veen, A., Schultze, M., Duffek, A.: A study on arsenic and the heavy metals in the Mulde River system. Acta Hydroch. Hydrob. **33**(5), 475–491 (2005)

Ko, I., Kim, J., Kim, K.: Arsenic speciation and sorption kinetics in the As–hematite–humic acid system. Colloids Surf. A **234**, 43–50 (2004)

Loukidou, M.X., Matis, K.A., Zouboulis, A.I., Liakopoulou-Kyriakidou, M.: Removal of As(V) from wastewaters by chemically modified fungal biomass. Water Res. **37**, 4544–4552 (2003)

Mamindy-Pajany, Y., Hurel, C., Marmier, N., Romeo, M.: Arsenic adsorption onto hematite and goethite. C. R. Chimie **12**, 876–881 (2009)

McComb, K.A., Craw, D., McQuillan, A.J.: ATR-IR spectroscopic study of antimonite adsorption to iron oxide. Langmuir **23**, 12125–12130 (2007)

Mikutta, C., Kretzschmar, R.: Spectroscopic evidence for ternary complex formation between arsenate and ferric iron complexes of humic substances. Environ. Sci. Technol. **45**, 9550–9557 (2011)

Mohan, D., Pittman Jr, A.U.: Arsenic removal from water/wastewater using adsorbents: a critical review. J. Hazard. Mater. **142**, 1–53 (2007)

Moller, T., Sylvester, P., Shepard, D., Morassi, E.: Arsenic in groundwater in New England: point-of-entry and point-of-use treatment of private wells. Desalination **243**, 293–304 (2009)

Nemade, P.D., Kadam, A.M., Shankar, H.S.: Adsorption of arsenic from aqueous solution on naturally available red soil. J. Environ. Biol. **30**(4), 499–504 (2009)

Parga, J.R., Vazquez, V., Moreno, H.: Thermodynamic studies of the arsenic adsorption on iron species generated by electrocoagulation. J. Metallurgy (2009). doi:10.1155/2009/286971

Partey, F., Norman, D., Ndur, S., Nartey, R.: Arsenic sorption onto laterite iron concentrations: temperature effect. J. Colloid Interface Sci. **321**, 493–500 (2008)

Payne, K.B., Abdel-Fattah, T.M.: Adsorption of arsenate and arsenite by iron treated activated carbon and zeolites: effects of pH, temperature, and ionic strength. J. Environ. Sci. Health **40**, 723–749 (2005)

Pokhrel, D., Viraraghavan, T.: Arsenic removal from an aqueous solution by a modified fungal biomass. Water Res. **40**, 549–552 (2006)

Rodriguez-Lucena, P., Lucena, J.J., Hernandez-Apaolaza, L.: Relationship between the structure of Fe-lignosulfonate complexes determined by FTIR spectroscopy and their reduction by the leaf Fe reductase. The Proceedings of the International Plant Nutrition Colloquium XVI UC Davis. eScholarship University of California, 1–4, Sacramento, CA, 26–30 August (2009)

Schweitzer, G.K., Pesterfield, L.L.: The Aqueous Chemistry of the Elements. Oxford University Press, New York (2009)

Smedley, P.L., Kinniburgh, D.G.: A review of the source, behavior and distribution of arsenic in natural waters. Appl. Geochem. **17**, 517–568 (2002)

Steely, S., Amarasiriwardena, D., Xing, B.: An investigation of inorganic antimony species and antimony associated with soil humic acid molar mass fractions in contaminated soils. Environ. Pollut. **148**, 590–598 (2007)

Sun, H. (ed.): Biological Chemistry of Arsenic, Antimony and Bismuth. Wiley, Singapore (2011)

Thirunavukkarasu, O.S., Viraraghavan, T., Subramanian, K.S.: Removal of arsenic in drinking water by iron oxide-coated sand and ferrihydrite: batch studies. Water Qual. Res. J. **36**(1), 55–70 (2001)

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

Wang, X., Liu, G., Zhou, J., Wang, J., Jin, R., Lv, H.: Quinone-mediated reduction of selenite and tellurite by *Escherichia coli*. Bioresour. Technol. **102**, 3268–3271 (2011)

Wilson, S.C., Lockwood, P.V., Ashley, P.M., Tighe, M.: The chemistry and behavior of antimony in the soil environment with comparisons to arsenic: a critical review. Environ. Pollut. **158**, 1169–1181 (2010)

Xi, J., He, M., Lin, C.: Adsorption of antimony(V) on kaolinite as a function of pH, ionic strength and humic acid. Environ. Earth Sci. **60**, 715–722 (2010)

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

Zhang, F., Itoh, H.: Iron oxide—loaded slag for arsenic removal from aqueous system. Chemosphere **60**, 319–325 (2005)

Zhang, L., Zhang, M., Guo, X., Liu, X., Kang, P., Chen, X.: Sorption characteristics and separation of tellurium ions from aqueous solutions using nano-TiO_2. Talanta **83**, 344–350 (2010)