Biomaterial Sorbents for Antimony and Tellurium Removal

Linda Ansone, Maris Klavins
Department of Environmental Science, University of Latvia
Raina Blvd 19, Riga, Latvia
linda_ansone@inbox.lv; maris.klavins@lu.lv

Maruta Jankevica
Faculty of Chemistry, University of Latvia,
Raina Blvd 19, Riga, Latvia
maruta.jankevica@gmail.com

Abstract The present work investigates antimony and tellurium sorption using iron modified natural materials (peat, straw, shingles, moss, canes and sand). Results were obtained using batch tests and the sorption was studied as a function of initial metalloid concentration, pH, temperature and presence of competing substances. The optimal pH interval for sorption of Sb (III) is 6.5 – 9 and 3 – 6 of Sb (V), while tellurium sorption using Fe-modified materials is favourable in wider interval 3 – 9. The impact of temperature on the metalloid sorption capacity of Fe-modified peat was tested at four temperatures: 275 K, 283 K, 298 K, 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: Biomaterial sorbents, Antimony, Tellurium, Metalloids, Sorption.

1. Introduction
A large number of recent studies have been dedicated to environmental pollution with metalloid compounds. The most studied metalloid is arsenic, but increasingly more attention is paid also to antimony. At the same time, considerably less attention has been paid to tellurium. Nevertheless, it is important to study the occurrence of metalloids in the environment, as well as environmental pollution and possible methods for environment remediation.

Antimony is one of the toxic elements which occur in the environment as a result of human activities, for example, a product of anthropogenic activities, and as a result of natural processes, for example in natural waters as a product of natural weathering and erosion (Rakshit et al., 2011). Its concentration in non-polluted natural waters is usually lower than 1 mg/L, (Filella et al., 2002). The World Health Organization (WHO) guidelines the antimony concentration as 0.005 mg/L in drinking waters.

Antimony can occur in a variety of oxidation states (–3, 0, +3, +5) but mainly exist in two oxidation states (+3 and +5) in environmental, biological and geochemical samples. In the pH range of 2–11 antimony exists primarily as antimonate [Sb(OH)$_6$]$^-$ in oxidizing environments and antimonite [Sb(OH)$_3$], in reducing environments (Filella et al., 2002). In aqueous solution Sb(III) is available as [SbO]$^+$ and [Sb(OH)$_2$]$^+$ species at pH< 3. [HSbO$_3$] and [Sb(OH)$_3$] species are predominant at pH 3–10 and [SbO$_2$]$^-$ specie is existing in aqueous solution at pH> 10 (Uluozlu et al., 2010).

Because of the toxicological effects of antimony, its monitoring and subsequent removal from aqueous solution has been mandatory. Sorption to soil components is a major mechanism of Sb retention in the environment. A number of studies have investigated the sorption behavior of Sb on hydroxides of Fe, Mn, Al, humic acids, and clay minerals. Agriculture as well is one of the richest sources for low-cost adsorbents. Some studies demonstrated that both Sb (III) and Sb (V) can strongly bind to Fe hydroxides, and pH had a strong influence on Sb adsorption (Rakshit et al., 2011).
Tellurium is considered to be rare and non-essential element and it usually occurs at low concentration levels ($10^{-6}$%). Despite tellurium is widely distributed in trace amounts in the Earth crust, its toxicity can induce local environmental problems (Narukawa 1998). Toxicity of Te 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).

Up to now, studies on tellurium and its compounds in the environment are scanty, and the main attention in the existing studies has been focused on tellurium pollution near main tailing and industrial areas (Zhang et al., 2010). Tellurium compounds have been found in a wide range of different matrices, for example, clinical, biological, geological and others, but it is always in very low concentration, for example concentrations of Te in natural waters is generally at the sub-ppt level and therefore determination of Te often is difficult task as well as the behaviour of tellurium in nature is almost unknown. Tellurium can exist in 4 oxidation states (-2, 0, +4 and +6) in the environment. Aqueous Te species mainly exist in the form of oxyanions – tellurite (TeO$_3^{2-}$) and tellurate (TeO$_4^{2-}$) or hydroxide anions (Te(OH)$_{n}$, TeO(OH)$_{n-1}$). Te (VI) is the predominant form in aqueous species under oxic conditions, whereas Te (IV) predominates under reducing conditions (Harada and Takahashi 2009, Narukawa 1998). It is suggested that H$_5$TeO$_6$ is the main form of tellurium in aqueous environment in the pH range 7.5 – 11, while H$_6$TeO$_6$ is the predominant form at pH < 7.7 (Hein et al., 2003; Schweitzer and Pesterfield 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. Some studies have demonstrated that inorganic forms of antimony as well as tellurium 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.

Iron modified biomaterial (peat, shingles, straw, moss, canes and sand) sorbents were synthesized. The synthesis method was based on impregnation of the material with Fe oxohydroxide, followed by thermal treatment. Specific surface area measurements, as well as determination of pH$_{zpc}$, organic substances content and Fe$_2$O$_3$ analyses were used to characterize the sorbents and to assess the success of the modification methods. The surface area was measured using a surface area pore size analyser Gemini2360. The BET method was used for the specific surface area measurements. The pH$_{zpc}$ was determined by immersion technique (Fiol and Villaescusa, 2009). For the determination of organic matter, the loss-on-ignition (LOI) method was used. (Heiri et al. 2001). The Fe$_2$O$_3$ content 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. 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).

Sorption experiments were carried out using Fe- modified biomaterials. Inorganic forms of antimony – potassium hexahydroxooantimonate (V) and potassium antimonyl tartrate as well as inorganic forms of tellurium – potassium tellurite hydrate and telluric acid were used. Sb and Te concentrations were determined using FAAS (flame atomic adsorption spectrometry). The obtained sorption data were correlated using the Langmuir and Freundlich isotherm models.

To investigate the impact of physicochemical conditions on antimony or tellurium removal, sorption experiments were carried out at different temperatures (275 K, 283 K, 298 K and 313 K), to investigate the impact of pH, 0.1 M HCl and 0.1 M NaOH were used to obtain desired solution pH (pH interval 3 - 9).
3. Results and Discussion

3.1. Characterization of sorbents

As it was expected the content of organic matter for all analysed sorbents of an organic origin is similar and it varies form 74 % to 83 %, but Fe-modified sand shows considerably lower results – only 1.2 % (Table 1). Fe-modified peat has the highest Fe$_2$O$_3$ content and the highest specific surface area comparison to other in this study used sorbents. So that specific surface area is one of the most important parameters that may affect metalloid sorption capacity, and taking into account metalloid high affinity to interact with iron compounds, it is possible to predict that in this case Fe-modified peat will have the highest sorption capacity and it could be an effective sorbent for antimony and tellurium removal.

Table 1. Characterization of sorbents

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>LOI, %</th>
<th>Fe$_2$O$_3$, mg/g</th>
<th>Specific surface area (BET method), m$^2$/g</th>
<th>pH$_{zpc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-mod. peat</td>
<td>74</td>
<td>424.8</td>
<td>44.16</td>
<td>4.7</td>
</tr>
<tr>
<td>Fe-mod. shingles</td>
<td>83</td>
<td>297.7</td>
<td>45.31</td>
<td>5.5</td>
</tr>
<tr>
<td>Fe-mod. canes</td>
<td>79</td>
<td>274.8</td>
<td>40.31</td>
<td>7.0</td>
</tr>
<tr>
<td>Fe-mod. moss</td>
<td>80</td>
<td>256.5</td>
<td>19.14</td>
<td>3.2</td>
</tr>
<tr>
<td>Fe-mod. straw</td>
<td>81</td>
<td>292.3</td>
<td>-</td>
<td>5.3</td>
</tr>
<tr>
<td>Fe-mod. sand</td>
<td>1.2</td>
<td>49.4</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The pH of the point of zero charge ($\text{pH}_{zpc}$) is one of the parameters that characterize surface chemical properties of the studied materials. The pH of the point of zero charge is the pH above which the total surface of the sorbent is negatively charged, while at pH $<$ $\text{pH}_{zpc}$ surface has a positive charge (Al-Degs et al., 2007).

3.1. Antimony and Tellurium Removal

Sorption isotherms characterise the equilibrium partitioning between sorbed and desorbed phases, providing information about sorption process. The obtained sorption isotherms were compared with the sorption models of Langmuir and Freundlich. Based on correlation coefficients the obtained data best fitted to the Langmuir isotherm model (Eq. 1):

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

(1)

The constants $q_m$ and $K_a$ of the Langmuir equation can be determined from the linearized form of the Langmuir equation (Eq. 2):

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

(2)

where $C_e$ is the equilibrium concentration (mg/L), $q_e$ is the amount of metalloid sorbed onto solid phase (mg/g), $q_m$ is $q_e$ for a complete monolayer (mg/g), and $K_a$ is the sorption equilibrium constant (L/mg).

Antimony and tellurium sorption capacity is dependent on the biomass sorbent used, although reaction conditions for material modification with iron compounds were similar.

Unmodified natural materials, such as raw peat material, are not useful for neither antimony nor tellurium 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
The highest sorption capacity of Sb (III) was observed for Fe-modified peat sorbent, whereas Fe-modified canes and Fe-modified sand shows similar but not as high results.

For a better understanding, the sorbed amounts of antimony (III) at corresponding sorbate/sorbent ratios and experimental conditions were calculated to percentage. Fe-modified peat can sorb 95% at the initial concentration of 365 mg/L, and the sorbed amount of Sb decreases to 57% if initial Sb (III) concentration reaches 702 mg/L. The sorbed amounts of Fe-modified canes and Fe-modified sand exceed 97% and 59% accordingly if the initial Sb (III) concentration is 176 mg/L, whereas sorption capacity of Fe-modified moss and Fe-modified shingles, exceeds 95% and 83% accordingly if initial Sb (III) concentration is 283 mg/L. However, modified straw can be used effectively at lower Sb (III) concentrations – its sorption capacity exceeds 40% at the initial concentration of 280 mg/L.

Similarly to antimony (III), sorption capacity of antimony (V) using Fe-modified peat as a sorbent show the highest sorption efficiency if we compare in this study used sorbents. In addition, sorption capacity of Sb (V) is higher than that of Sb (III) – it reaches 44 mg/g in other words it may sorb more than 99% of Sb (III) at the initial concentration of 182 mg/L, and the sorbed amount of antimony (V) decreases to 75% if initial Sb (III) concentration reaches 727 mg/L. In contrast to Sb (III), efficiency of such sorbents as Fe-modified moss and Fe-modified shingles are similar and only slightly lower than 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 Fe-modified moss and Fe-modified shingles accordingly. Fe-modified straw can be used in less polluted areas. Fe-modified straw can sorb up to 57% of Sb (V) if the initial antimony concentration is 92 mg/L.

To sum up, the biosorbents used in this study are very effective in removing antimony (III) as well as antimony (V). Fe-modified peat is the most effective sorbent for Sb (III) and Sb (V) removal and it is possible to use this sorbent for waters severely polluted with antimony compounds. The sorption efficiency of Fe-modified moss, Fe-modified shingles and Fe-modified straw is similar for both forms of antimony and thus these sorbents can be applied in areas where antimony concentration is lower.

The results are quite different in case of tellurium (VI) removal (Fig. 2). Probably the reason could be the differences in sorbate structure and corresponding chemical properties. The sorption capacity of all Fe-modified sorbents except Fe-modified sand is similar and it varies from 14 to 18 mg/g; sorption capacity is little bit higher than 4 mg/g for Fe-modified sand. In other words Fe-modified peat can sorb about 98% of Te (VI) at the initial Te concentration of 50 mg/L and it decreases to 55% at the initial Te (VI) concentration of 400 mg/L. Similar trend was observed also for Fe-modified moss and Fe-modified straw.
canes. Fe-modified shingles as well as Fe-modified straw can sorb 99% of Te (VI) and 93% of Te (VI) at the initial Te concentration of 95 mg/L accordingly and sorption decreases to 46% for Fe-modified straw and to 49% to Fe-modified shingles as initial Te (VI) concentration increases to 391 mg/L.

![Graph](image)

**Fig. 2.** Te (VI) sorption using Fe-modified biomaterials as a sorbents, sorption time 24 h, room temperature.

Fe-modified moss and Fe-modified peat are the best sorbents for tellurium (IV) removal. Fe-modified peat can sorb 98% of Te (IV) at the initial concentration of 390 mg/L and Fe-modified moss can sorb 96% at the initial concentration of 390 mg/L. Fe-modified straw as well as Fe-modified canes could be used as effective Te (IV) sorbent in areas where Te (IV) concentration is lower – sorption efficiency reach 99% for Fe-modified straw and 95% for Fe-modified canes accordingly at the initial Te (IV) concentration of 96 mg/L.

To summarise, sorption capacity of sorbents used in this study is higher sorbing Te (IV) instead of Te (VI). Sorbed amount of tellurium (VI) for all used sorbent with exception of Fe-modified sand is similar and it varies from 45 to 55% at the initial Te (IV) concentration of 400 mg/L. But sorbed amount of Te (IV) differs more significantly if we compare sorption capacity of all in this study used sorbents. Sorbed amount of Te (IV) varies from 98% using Fe-modified peat to 50% using Fe-modified canes at the initial Te (IV) concentration of 400 mg/L.

Comparing sorption isotherms of Sb (III), Sb (V), Te (IV) and Te (VI) it is possible to notice that Fe-modified peat is the best sorbent for both forms of Sb as well as Te. 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 carboxyl groups and phenolic hydroxyls. Minor importance has amino groups, but also they might contribute to antimony and tellurium sorption. We can conclude that, 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. Considering into account both - obtained results as well as study of literature it could be concluded that the reason of such an outcome could be the formation of metalloid – oxygen – iron bond in Fe-modified sorbents, for example, Sb-O-Fe or Te-O-Fe. This assumption has also been confirmed by other studies that suggest that the solid phases loaded with Fe species can sorb metalloids, possibly due to the formation of stable inner and outer sphere surface complexes. For example, spectroscopic evidence using 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.
3.2. Different Parameter Impact on Sorption Process

pH is one of the most important parameters that affect sorption process. The sorption capacity of Fe-modified biomaterials sorbing Sb (V) is maximal at acidic pH values and sorption capacity decreases as pH value increases. As it is seen in Figure 3, the best pH interval for antimony (V) removal is 3 – 6.5 when Sb(OH)\(_6\)\(^{-}\) is the predominant form.

For the purpose of interpretation of the obtained data, it could be supposed that the sorption of Sb, as well as Te 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. pH has an impact on both the form of the element in the solution as well as ionization potential of active sorption sites. Surface charge of the sorbent is one of the most important parameters that may characterise protonation and deprotonation and thus gives significant information about sorption mechanism. As it was previously mentioned, the pH of the point of zero charge (pH\(_{\text{zpc}}\)) is one of the parameters that characterise surface chemical properties of the studied materials. The pH\(_{\text{zpc}}\) is the pH above which the total surface of the sorbent is negatively charged, while at pH < pH\(_{\text{zpc}}\) surface has a positive charge (Al-Degs et al., 2007). As it is seen in Table 1 pH\(_{\text{zpc}}\) values of studied sorbents varies from 3.2 to 5.5; for example pH\(_{\text{zpc}}\) of Fe-modified peat is 4.7, then surface of the sorbent is positively charged if pH < 4.7, and antimony is negatively charged, and the sorption capacity is maximal. At the pH interval pH > 4.7, surface of the sorbents become negatively charged and interaction between active sorption sites on the sorbent and negatively charged Sb(OH)\(_6\)\(^{-}\) ions decreases. The reason for decrease of sorption capacity in basic solution could be also competition for sorption sites between antimonite and hydroxide ions.

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

Fig. 3. pH influence on Sb (V) sorption using Fe-modified biomaterials as a sorbents, sorption time 24 h, room temperature (Sb (V) initial concentration 200 mg/L).

pH has not significant impact on both Te (IV) and Te (VI) removal at the studied conditions. As previously suggested, H\(_5\)TeO\(_6\) is the main form of tellurium (VI) in aqueous environment in the pH range 7.5 – 11, while H\(_6\)TeO\(_6\) 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 in the entire studied pH interval. The sorbed amount of Te (VI) increases from 55 to 90 % as pH value increases from 3 to 6 using Fe-modified shingles and similar trend was observed for Fe-modified straw. Fe-modified biomaterials may sorb more than 98 % of Te (IV) (Te 100 mg/L) in the pH interval (3 – 7), and sorbed Te amount only slightly decreases at pH >7.
Temperature is one of the factors that have an impact on the sorption process as well as it gives insight into the sorption mechanism. The impact of temperature on the antimony and tellurium sorption capacity of Fe-modified peat was tested at four temperatures: 275 K, 283 K, 298 K, 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 Te (VI) sorption is shown in Figure 4.

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

The Gibbs free energy ($\Delta G^0$), standard enthalpy ($\Delta H^0$), and standard entropy changes ($\Delta S^0$) are calculated using Eqs. 1, 2, and 3:

$$\Delta G^0 = -R \cdot T \cdot \ln K_a$$

(1)

$$\ln \left( \frac{K_{a1}}{K_{a2}} \right) = - \frac{\Delta H^0}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

(2)

$$\Delta G^0 = \Delta H^0 - T \Delta S^0,$$

(3)

where $K_a$ 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 Table 2.

**Table 2.** The calculated Langmuir constants and Gibbs free energy (sorbent – modified peat)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>K (L/mol)</th>
<th>$\Delta G$(kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sb (III)</td>
<td>Sb(V)</td>
</tr>
<tr>
<td>275</td>
<td>30000.0</td>
<td>10000</td>
</tr>
<tr>
<td>283</td>
<td>35454.5</td>
<td>14150</td>
</tr>
<tr>
<td>298</td>
<td>17647.1</td>
<td>20769.2</td>
</tr>
<tr>
<td>313</td>
<td>11666.7</td>
<td>32125</td>
</tr>
</tbody>
</table>
The negative $\Delta G^\circ$ values for the sorption of antimony and tellurium (Table 2) onto modified peat indicate that the metalloid sorption process is of a spontaneous nature. The fact that the values of $\Delta G^\circ$ become more negative with increase in temperature indicates more efficient adsorption at a higher temperature. Positive $\Delta H^\circ$ values (for example $\Delta H^\circ_{\text{Sb(V)}} = 21.98 \text{ kJ/mol}$, $\Delta H^\circ_{\text{Te(IV)}} = 32.15 \text{ kJ/mol}$), 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 ($\Delta S^\circ_{\text{Sb(V)}} = 156 \text{ J/mol} \cdot \text{K}$, $\Delta S^\circ_{\text{Te(IV)}} = 185 \text{ J/mol} \cdot \text{K}$) show increasing the degree of freedom of the adsorbed metalloid species onto modified peat. 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.

4. Conclusion

Impregnation of natural materials with Fe compounds significantly enhances the sorption capacity of sorbents and makes them useful for the removal of metalloids. Moreover, Fe-modified peat is the most effective sorbent for antimony and tellurium removal in this study and it is possible to use this sorbent for waters severely polluted with metalloids.

Fe-modified moss and Fe-modified shingles can effectively sorb all the studied metalloids, although Fe-modified straw and Fe-modified canes can also be used in areas where metalloid concentrations are low.

The sorption capacity increased with increase in temperature for all of the studied metalloids and the calculated thermodynamic parameters suggest that the sorption process is of a spontaneous nature and endothermic.

Acknowledgements

This work was supported by the European Social Fund within the project “Support for Doctoral Studies at the University of Latvia”.

References


Narukawa T. (1999) Separation and determination of tellurium (IV) and -9VI) by electrothermal atomic absorption spectrometry using a tungsten furnace after collection as the 3-phenyl-5-mercapto-1,3,4-thiadiazole-2(3H)-thione-tellurium complex on cobalt (III) oxide. J. Anal. At. Spectrom., 14, 75-80.


Schweitzer G.K., Pesterfield L.L. (2010). The aqueous chemistry of the elements, Oxford University Press, 434